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Role of clay minerals in the transportation of iron*

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Abstract—The clay minerals have iron associated with them in several ways: (1) as an essential constituent, (2) as a minor constituent within the crystal lattice where it is in isomorphous substitution and (3) as iron oxide on the surface of the mineral platelets. Nontronite, "hydromica," some chlorites, vermiculite, glauconite and chamosite contain iron as an essential constituent. Kaolinite and halloysite have no site within the lattice for iron, but in certain environments iron oxide (goethite or hematite) is intimately associated as a coating on the micelles. Analyses of clay minerals show that the content of Fe_2O_3 varies: 29 per cent (nontronite), 7·3 per cent (griffithite), 4·5 per cent ("hydromica"), 5·5 per cent (chlorite), 4 per cent (vermiculite) and 18 per cent (glauconite). The FeO content is: 40 per cent (chamosite), 7·8 per cent (griffithite), 1–2 per cent ("hydromica"), 3 per cent (glauconite) and 2 per cent (chlorite).

The iron associated with the clay minerals remains stable in the environment in which the minerals occur, but if either pH or Eh or both are changed the iron may be affected. Change of environment will cause: (1) removal of iron by reduction of Fe^{3+} to Fe^{2+}; (2) ion-exchange reactions; (3) instability of the crystal lattice.

Experiments using bacterial activity to produce reducing conditions with kaolinite and halloysite coated with iron oxides and with nontronite in which ferric iron is in the octahedral position within the lattice showed that ferric oxide is removed at Eh +0·215 in fresh water and at Eh +0·098 in sea water. Hematite, goethite, and indefinite iron oxides were removed at different rates. Red ferric oxides were changed to black indefinite noncrystalline ferrous sulphide at Eh −0·020 but reverted to ferric oxide under oxidizing conditions. Nontronite turned bright green under reducing conditions and some of the ferrous iron remained within the lattice on a return to oxidizing conditions. Bacterial activity seems to be necessary for maintaining reducing conditions in the environments studied.

INTRODUCTION

THERE is a considerable literature on the transportation of iron and on its deposition in the form of bedded iron ores such as the Clinton (ALLING, 1947) and the Northampton sand ironstone formation (TAYLOR, 1949), and as iron associated with other rock constituents. There seems to be no doubt that this iron was derived from the weathering of rocks and that it was transported to the sites of deposition. There is doubt, however, about the method of transportation. TAYLOR (1949, p. 80) has discussed the divergent opinions as to the chemical state in which iron is transported. Some workers have postulated that iron is carried mainly as ferrous bicarbonate, whereas others think that it may be carried as a ferrous salt of silicic, carbonic, sulphuric, hydrochloric or other acids, including organic acids. It is probable that all or many of these anions are associated with iron in certain environments, variation being caused by local conditions of drainage, pH, and Eh. CASTANO and GARRELS (1950) have shown experimentally that iron introduced as ferrous chloride into a 3·5 per cent aerated solution of sodium chloride will be precipitated as ferric oxide.

In addition to the chemical transportation of iron, there is a mechanical method of transportation and deposition that depends on the association of iron with the clay minerals. It is the purpose of this paper to consider in some detail

* Publication authorized by the Director, U.S. Geological Survey.

the association of iron with the clay minerals and the means whereby it may be removed from these minerals in certain environments.

IRON CONTENT OF CLAY MINERALS

Iron may be associated with the clay minerals in two different ways: within the clay mineral structure iron may be an essential ion, as in nontronite, or a substitute ion, as in some members of the montmorillonite group. External to the clay mineral structure iron is very commonly present as an oxide adhering to the surfaces of the particles. Adhering iron oxide is one of the effects of weathering and soil-forming processes and it is therefore an indication of environment.

Iron as a constituent of the clay mineral structure

Many of the clay minerals contain iron as an essential constituent; others have crystal lattices in which the structure allows the presence of the Fe^{3+} or Fe^{2+} ion. Table 1 lists selected analyses of clay minerals taken from several published sources. The clay minerals containing iron as an essential constituent are: "hydromicas," nontronite, griffithite, some chlorites, vermiculite, chamosite and glauconite.

The site of the iron ion depends on the nature of the clay mineral lattice. In the more complex lattices—the 2–1 layer types (mica group)—the iron ion is in the octahedral layer. In kaolinite (and halloysite) there is normally no site within the lattice for iron, but under certain conditions the mineral chamosite, with the structure of either kaolinite or chlorite, forms and would seem to be the expression of the environmental conditions under which structures with a site for the Fe^{2+} ion exist. One of the requirements is a low pH and reducing conditions rather than oxidizing. The chamosite found in the highly weathered zone of basaltic rocks changing to laterite and bauxite (EYLES, 1952, p. 50) is due to percolating ground waters which reduce the iron to the ferrous state. In oxidizing conditions the ferrous iron changes to ferric, and limonite results, as has been observed in the Northampton ironstones by TAYLOR (1949, p. 20).

Iron oxide on the surfaces of clay mineral particles

In addition to the iron within the clay mineral lattice, in certain environments iron oxides occur as coatings on the surfaces of the clay micelles. Particularly noticeable in this respect are the kaolinitic clays of the tropics with their bright-red coloration due to hematite and other oxides. The colour of any yellow, brown or red soil is due to iron oxides such as goethite, lepidocrocite, hematite or indefinite iron oxides with poor crystallinity. Such oxides are nearly always associated with the clay minerals, although films of oxide may also coat mineral grains of the sand and silt grades as well as those of the clay fraction ($<2\ \mu$).

The association of iron in the form of an oxide with the clay minerals is one of the most common features of rock weathering and soil formation. The presence of iron oxide is an expression of an oxidizing environment, for where the environment is reducing the iron will be in the ferrous state and will be colourless or grey instead of red or brown.

Analyses of the clay fractions of soils show that the iron is mainly associated

Table 1. Iron content of certain clay minerals*

Mineral	Fe_2O_3 (%)	FeO (%)	Position in crystal lattice
(1) Kaolinite	0·27	0·06	In addition, free iron oxides adhere to the flat surfaces of the hexagonal sheets in amounts regulated by the pH of environment
(2) Halloysite	0·11	0·01	Probably similar to kaolinite
(3) Allophane	variable		Probably an irregular association
(4) Chamosite, ferric	0·22	39·79	Octahedral layer
Chamosite, artificial	43·37	0·45	
(5) Hydrous mica ("illite")	4·59	1·70	Generally in the octahedral layer, but may be in tetrahedral layer
(6) Glauconite	18·0	3·1	Octahedral layer
(7) Celadonite	17·19	4·02	Octahedral layer
(8) Montmorillonite†	0·83	—	Octahedral co-ordination
(9) Nontronite†	29·57	0·71	Octahedral co-ordination
(10) Griffithite	7·32	7·83	Octahedral co-ordination
(11) Vermiculite	4·24	0·68	Octahedral co-ordination
(12) Chlorite group	5·52	1·95	Octahedral layer or in brucite lay between the mica layers
(13) Attapulgite	3·53	—	

* Data from published analysis.
† The montmorillonite group is represented by two end-members and griffithite.

(1) Macon, Ga (Kerr *et al.*, 1950, p. 43).
(2) Bedford, Ind. (Kerr *et al.*, 1950, p. 48).
(3) No locality.
(4) Corby, Northamptonshire, England (Brindley and Youell, 1953, p. 61).
(5) Fithian Ill. (Grim and Rowland, 1942, p. 759).
(6) Norwalk, Wis. (Hendricks and Ross, 1941, p. 692).
(7) Reno, Nev. (Hendricks and Ross, 1941, p. 697).
(8) Montmorillon, France (Ross and Hendricks, 1945, p. 34).
(9) Spokane, Wash. (Ross and Hendricks, 1945, p. 35).
(10) Cahuenga Pass, Los Angeles, Calif. (Faust, 1955, p. 67).
(11) Bare Hills, Md. (Gruner, 1934, p. 559).
(12) Brinton Quarry, West Chester, Pa. (McMurchy, 1934, p. 422).
(13) Attapulgus, Ga. (Bradley, 1940, p. 405).

with the finest fractions (the clay and silt grades), which have an extremely large surface area. Baver (1956, p. 12) has calculated that the number of particles of clay 2 μ in diameter equal to the amount in a sphere 1 cm in diameter is 125×10^9; the area of these is 15,708 cm^2 or 16·9 ft^2. Much of the iron in the clay fractions is in an easily removable form which is generally referred to as free iron oxide by soil chemists; this iron has been much studied because of its importance in connexion with such soil processes as podzolization and gleying. The free iron oxide in the clay fractions of various parts of a Frederick silt loam developed on limestone averages 6·8 per cent (Carroll and Hathaway, 1954, p. 174). The clay fraction is recognized by van Straaten (1954) as being the principal source of the iron in the sediments of the Wadden Sea, Holland. Alexander, Byers and Edgington

(1939, p. 16–17) reported an average ferric oxide content of 11·21 per cent in fifty-three colloid fractions of soils from limestones in the Appalachian Valley in Maryland and Virginia. The average ferric oxide content of the colloid fraction of 162 soils from various parts of the United States, including the Mississippi River drainage basin, is 10·3 per cent (Anderson, Keyes and Cromer, 1942; Brown and Thorp, 1942; Holmes and Hearn, 1942).

Iron on the surfaces of clay minerals, principally kaolinite, has been studied in considerable detail by Fripiat and Gastuche (1952). The iron is in the form of ferric oxide which varies according to the environment and the exchangeable cations present. Thus, if kaolinite is in the H-form the complex of kaolinite oxide has a porous, disordered structure with an indefinite capacity for the absorption of oxide (the pH will be low and the kaolinite will be in equilibrium with its environment), whereas if the exchangeable cations are Na, K, Ca or Mg, the kaolinite-oxide complex is compact, ordered and non-porous; the surface is saturated rapidly and pure iron oxide particles are formed. Moreover the iron oxide accumulates in definite quantities which were found experimentally to be equivalent to ten times the cation-exchange capacity. Thus, a kaolinite of cation-exchange capacity of 5 meq/100 g would be able to accumulate 50 meq Fe^{3+}/100 g. This is a considerable quantity of iron and the mechanism is certainly of geological importance in the movement of iron. This latter association of iron oxide with kaolinite requires a higher pH than if the kaolinite were in the H-form, and kaolinite is not stable for indefinite periods at pH above neutral. Although no investigations have been made of iron oxide on the surfaces of other clay minerals, probably it does exist in this way, as it can be readily removed by chemical methods and is reported as free iron oxide (Deb, 1950). Kaolinite is, however, the most stable of the clay minerals, and in some environments montmorillonite, for example, would break down so that the relationship with this oxide would be difficult to assess.

Clay Minerals and Their Environments

Mechanical transportation of iron with the clay minerals is almost entirely the work of rivers although movement of fine material by wind, resulting in the deposition of loess, is important in many areas. The kinds of clay minerals transported and their relationship with iron oxides will depend on the environment in which they occur.

It has been recognized that certain clay minerals are characteristic of certain environments, a fact first pointed out clearly by Millot (1952), although others had recognized the significance of the various associations. In Table 2 are listed the various clay minerals, their environment, pH of most common environment, and cation-exchange capacity. All these facts are of importance in considering weathering processes and stability of the clay minerals, and hence their potentialities as constituents of sediments arising as a result of transportation. The matter of environment is a complex one, for soils from different climatic and geographic regions will contain different clay minerals. Some insight can be obtained from areas where old soils that developed under different climatic conditions can be recognized as distinct from those soils now developing. Such are the red and the

black soils developed on basaltic rocks in parts of eastern Australia (HALLSWORTH, 1951; FERGUSON, 1954). Stability conditions can be obtained for many of the clay minerals from observation of their environments, but care is needed in interpretation because of differences in rates of weathering; thus if many mixed-layer mica–montmorillonite, chlorite–vermiculite or other mixtures occur it would seem to indicate that the clay minerals are in process of adjusting to their environment. The weathering sequence of JACKSON and others (1948) is probably an

Table 2. Environmental types of clay minerals

Mineral	Environment	Conditions of formation	pH	Exchange capacity* (meq/100 g)
Kaolinite	Soils, mineral veins	Leaching, oxidizing or reducing	4+	3–15
Halloysite	Soils, mineral veins	Leaching, particularly where oxidizing sulphides have supplied H_2SO_4; moist	3–4	5–10 ($2H_2O$) 40–50 ($4H_2O$)
Allophane	Soils, mineral veins	Similar to kaolinite or halloysite	4	70
Chamosite	Marine and in laterites		low	not known
Hydrous mica ("illite")	Soils and marine sediments; shales	Apparently fairly wide range of conditions; occurs as a transition type, but not under intense leaching. Fixes K and other ions	not very critical	20–40
Glauconite	Marine	Near-shore environment; stagnant water containing only a little sulphide		20 (approx.)
Celadonite	Alteration product	Various	?	?
Montmorillonite group	Soils, bentonites, mineral veins, shales	Neutral or alkaline conditions unstable under acid leaching	7+	80–100
Vermiculite	Soils, altered biotite	Apparently a fairly wide range of conditions	not very critical	100–150
Chlorite	Rocks, soils, marine	Apparently a fairly wide range of conditions, but more stable in alkaline conditions	probably 7+	10–40 ?
Attapulgite	Lakes in arid environments; soils	Dry, alkaline	8+	20 (approx.)

* Exchange capacity measured at pH 7.

expression of the evolution of the soil clay minerals toward equilibrium with the environment.

As the pH of soils is important because of its influence on the type of clay mineral that will be in equilibrium under conditions of climate, topography, temperature and microbiological activity, so the redox potential is important because of its influence on the oxidation of the iron present. The stability fields for ferrous and ferric ions have been discussed by KRUMBEIN and GARRELS (1952, p. 10); the ferric–ferrous ratio is controlled by Eh. In the range of normal soils hematite, and presumably goethite, lepidocrocite and indefinite iron oxides, occur under oxidizing conditions with Eh above +0·150 V. STARKEY and WIGHT (1945) have shown in a number of soils that the critical value of Eh is approximately 0·100 V; below that figure corrosion of steel pipes occurs, this being partly due

to bacterial action, a point that will be discussed in another section of this paper. Thus, in soils having an Eh reading below +0·100 V, the migration of iron in the ferrous state may take place. This leads to some interesting and important features of the transportation and deposition of iron. Under oxidizing conditions ferric oxides, whether present as definite minerals on the clay micelles or as indefinite oxides, will remain attached to the clay, but where the redox potential is lowered the ferric iron changes to the ferrous state and goes into solution.

REMOVAL OF IRON FROM CLAY MINERALS

Two main factors are to be considered in the transportation and deposition of iron in its association with the clay minerals. The first factor is the stability field for ferric and ferrous iron, which has already been mentioned. The second factor is the stability of the clay minerals in certain environments. The redox potential determines the condition under which iron is removed from the outside of the clay micelles, and it also can influence the behaviour of ferric iron within the mineral lattice to a certain extent, as will be described for nontronite. The stability of the clay mineral lattices depends on the ability of ions in the environment either to remain in equilibrium with the mineral or to replace the exchangeable ions. Thus, where hydrogen ions replace metallic cations, the mineral tends to become unstable; loss of potassium ions results in the production of hydrous mica from muscovite-type mica.

Laboratory studies of the methods of removal of iron oxides from clay minerals were made with regard to the mechanisms found in natural environments. Three environments were examined: (1) freshwater anaerobic, (2) marine aerobic, and (3) marine lagoon-type anaerobic. In addition the stability of various clay minerals in sea-water with and without added hydrogen sulphide was studied. Three samples of kaolinite and halloysite coated with iron oxide were used, and the iron on the outside of clay micelles was removed in a manner similar to that which occurs in nature. Other samples used were A.P.I. standard minerals.

Removal of iron oxide from the surfaces of clay mineral particles

In the laboratory there are several ways to remove iron oxide films from the surfaces of clay minerals. This iron is known to soil scientists and chemists as free iron oxide, and its removal facilitates the examination of clay minerals by X-ray and other means. In addition the amount of free iron oxide present is important in a number of soil-forming processes such as podzolization, laterization and gleying. DEB (1950) has outlined the methods for its removal. Some of these methods are dependent on acid reactions, some on the reduction of iron from the ferric to the ferrous state. The amount of free iron oxide varies; DEB (1950, p. 215) gives figures of 7·6, 9·6, 2·2 and 26·5 per cent for samples of soil from England, Africa and India. CARROLL and HATHAWAY (1954) found between 3 and 9 per cent in samples from a soil profile on limestone in Virginia.

Of particular importance from the point of view of sedimentation is DROSDOFF and TRUOG's method (1935) for the removal of free iron oxide in which clays under alkaline conditions are saturated with hydrogen sulphide and the iron is converted to ferrous sulphide. The iron is first reduced from the ferric to the ferrous state.

In another method for removing ferric oxide coatings from sand and silt particles, JEFFRIES (1946) used nascent hydrogen to reduce the ferric iron to the ferrous state. The nascent hydrogen is formed by the reaction of metallic magnesium in a warm acid solution of potassium oxalate. Both methods are dependent on the Eh of the solution and independent of the pH (DEB, 1950, p. 215; KRUMBEIN and GARRELS, 1952, p. 17) under the somewhat acid conditions produced.

Another method of considerable importance is the removal of iron by anaerobic bacteria in the presence of sucrose or other carbohydrates; fermentation by soil bacteria causes a reduction in the Eh and a decrease in the pH of the solution, accompanied by the formation of organic acids. In a colloidal suspension of clay, the clay is first flocculated as a result of organic acid production which reduces the pH; CO_2 produced in sucrose decomposition initiates this process. The Eh is then reduced, and Fe (III) goes into solution as Fe^{2+}, which in the dilute solutions formed is colourless. If the fermentation is continued and the gases are not allowed to escape, the ferrous iron in solution may change back into the ferric state and the solution turns yellow. This reaction may be due to the effect of the acids formed during fermentation, as suggested by ALLISON and SCARSETH (1942) who first described this method of removing iron oxide films from clay minerals. The final result is that the bright-red colour of a clay is bleached to grey or white.

Much has been written concerning the activities of the iron-depositing bacteria (HARDER, 1919), the soil bacteria (WRIGHT, 1922; STARKEY and HALVORSON, 1927) and the sulphur-depositing bacteria (ZoBELL, 1946), but there is little about the action of soil bacteria in mobilizing iron by changing it from the ferric to the ferrous state, although ALLISON and SCARSETH's method (1942) for the removal of free iron oxide is based on such a reaction. BROMFIELD (1954) has, however, described a series of experiments on the bacterial reduction of iron by soil bacteria following the work of STARKEY and HALVORSON (1927) and of BLOOMFIELD (1950).

Bacterial action in freshwater, anaerobic conditions. An experiment using ALLISON and SCARSETH's (1942) method was set up using one sample of kaolinite, two samples of halloysite and one of nontronite. Particulars of these samples are:

Kaolinite Y-3, Clay fraction ($<2\ \mu$) separated from old red residual soil collected by J. T. HACK on County road 796 near Oak Grove Church, 4·2 miles NNW of Waynesboro, Augusta County, Waynesboro quadrangle, Virginia.

Halloysite 1-2, Clay fraction ($<2\ \mu$) separated from Chacha clay on Mariana limestone, collected by C. H. STENSLAND, about 2·5 miles SE of Agana, Guam. Depth, 6–8 in. (Lat. 13° 27′ 51″ N; Long. 144° 48′ 25″ E).

Halloysite 6-2, Clay fraction ($<2\ \mu$) separated from Atate clay on volcanic tuff and coglomerate, collected by C. H. STENSLAND about 2·5 miles south of centre of Talofofo village, Guam. Depth, 2–10 in. (Lat. 13° 18′ 38″ N; Long. 144° 44′ 45″ E).

Nontronite, H33a, A.P.I. standard. Garfield, near Spokane, Washington.

Various properties of these minerals are given in Table 3.

The clay fractions of kaolinite and of the two samples of halloysite were made by G. W. CHLOE, U.S. Geological Survey, from the original soils by shaking and dispersing the soils in distilled water without using any dispersing agent. The nontronite sample was crushed to pass a 270 mesh (0·053 mm) sieve. A 1 g sample of each clay was dispersed in distilled water and placed in a 250 ml Erlenmeyer

Table 3. Colour, free iron oxide, crystallinity, ion-exchange capacity, pH and form of the iron oxides in the clay minerals used in bacterial experiments

Mineral	Colour (Munsell chart)	Free iron oxide (%)	Crystallinity*	Ion-exchange capacity (meq/100 g)	pH	Iron oxides present†
Kaolinite Y-3	2·5 YR 6/8	15·4	Poor	17·2	5·90	Goethite, hematite
Halloysite 1-2	10 YR 6/8	14·0	Poor	15·0	6·20	Goethite, hematite
Halloysite 6-2	5 YR 5/8	13·2	Poor	21·4	5·35	Hematite, goethite, indefinite Fe_2O_3
Nontronite H33a	5 Y 8/4	—	—	99·5	7·20	Fe_2O_3 in octahedral position in lattice

* Determined from electronmicrographs made by J. C. HATHAWAY.

† Determined from X-ray diffraction patterns made by J. C. HATHAWAY.

Other determinations were made by the author.

Note: The rather high ion-exchange capacity for kaolinite is probably due to its disordered structure. The figures for halloysite are higher than those for the $2H_2O$-form (metahalloysite) but not high enough for the $4H_2O$-form (endellite).

flask; water was added to bring the volume up to 200 ml. A bacterial inoculant was made by shaking up a local soil in distilled water on an end-over-end shaker for about $\frac{1}{2}$ hr, then removing part of the dispersed clay. This was centrifuged in a high-speed head to remove the clay, leaving a clear supernatant in which bacteria were proved to be present by growth on a gelatine plate. A volume of 5 ml of this inoculant, together with 0·2 g sugar, was added to the clay-water mixtures in the flasks. The flasks were stoppered and a small rubber tube placed to lead from the top of each flask to a beaker of water. This was done so that the conditions would be anaerobic once the bacterial fermentation with its production of carbon dioxide had started. All the CO_2 was able to escape via the tube but no air could enter the flask. Eh and pH readings were made every day by removing a small sample from the flasks; observations on the appearance of the clay samples were made. The results of this experiment are tabulated in Table 4 and illustrated in Fig. 1. The experiment was continued for 19 days for nontronite and 27 days for the other three clays.

Observations were made on the appearance of the clay-water suspensions as a result of bacterial activity. This was most marked in the kaolinite and two halloysite samples, possibly because of additional bacteria which were already associated with these clays. ALLISON and SCARSETH (1942, p. 617) found that it was not necessary to use an inoculant for the bacterial removal of iron oxides from the colloidal clays that they used. The reaction with nontronite was much slower, but sugar in water without inoculation with bacteria failed to reveal any changes in the nontronite, and by the time the experiments were ended bacterial action was fairly brisk in the flask containing nontronite.

Within 2 days bacterial activity started within the flasks and after about 3

Table 4. Relation of pH and Eh during removal of ferric oxide coatings from clay particles by soil bacteria, under anaerobic conditions in fresh water*

Date	3 August 1956		6 August 1956		7 August 1956		8 August 1956		10 August 1956	
	pH	Eh	pH	Eh	pH	Eh	pH	Eh	pH	Eh
Kaolinite, Y-3	6·45	+0·350	5·85	+0·465	5·45	+0·366	4·0	+0·347	5·0	+0·225
Halloysite, 1-2	6·25	+0·460	5·82	+0·395	4·30	+0·255	4·20	+0·265	4·65	+0·250
Halloysite, 6-2	5·10	+0·450	5·85	+0·443	4·70	+0·470	3·65	+0·495	5·55	+0·325
Nontronite, H33a	7·0	+0·465	6·40	+0·445	5·30	+0·477	4·80	+0·415	6·25	+0·335

Date	11 August 1956		13 August 1956		14 August 1956		15 August 1956		16 August 1956	
	pH	Eh	pH	Eh	pH	Eh	pH	Eh	pH	Eh
Kaolinite, Y-3	5·50	+0·180	5·0	+0·175	4·80	+0·130	4·70	+0·145	4·75	+0·220
Halloysite, 1-2	4·80	+0·225	4·45	+0·220	4·10	+0·144	4·0	+0·185	4·05	+0·220
Halloysite, 6-2	5·73	+0·300	5·30	+0·230	5·02	+0·185	4·92	+0·215	5·0	+0·235
Nontronite, H33a	6·10	+0·305	5·75	+0·285	5·50	+0·280	5·50	+0·280	5·65	+0·305

Date	17 August 1956		20 August 1956		21 August 1956		22 August 1956		23 August 1956	
	pH	Eh	pH	Eh	pH	Eh	pH	Eh	pH	Eh
Kaolinite, Y-3	4·7	+0·165	4·57	+0·190	2·55	+0·460	4·55	+0·270	4·42	+0·280
Halloysite, 1-2	4·05	+0·190	4·95	+0·190	4·0	+0·264	4·0	+0·267	3·98	+0·175
Halloysite, 6-2	4·81	+0·174	4·89	+0·205	4·61	+0·223	4·65	+0·215	4·74	+0·203
Nontronite, H33a	5·35	+0·200	5·12	+0·443	5·21	+0·235				

Date	24 August 1956		27 August 1956		28 August 1956		29 August 1956	
	pH	Eh	pH	Eh	pH	Eh	pH	Eh
Kaolinite, Y-3	4·29	+0·256	4·20	+0·285	4·08	+0·305	3·95	+0·380
Halloysite, 1-2	3·92	+0·205	3·82	+0·251	3·70	+0·269	3·82	+0·360
Halloysite, 6-2	4·57	+0·237	4·42	+0·335	4·49	+0·325	4·80	+0·315

* 1 g clay, 0·1 per cent sucrose in 200 ml distilled water, inoculated with soil bacteria; kept at 25°C.

days the kaolinite and the two halloysite samples flocculated and bacterial action increased. Small additional quantities of sugar were added every 2–3 days. The supernatant became clear and colourless if the gas forming, presumably CO_2, was allowed to escape. The pH of the solution became lower and the Eh was also reduced (Table 4). The nontronite sample did not stay dispersed for as long as the other clay samples and there were no signs of bacterial action, although the pH and Eh figures were steadily lowered. After 8 days, bleaching of the red and yellow iron oxide coatings on the kaolinite and halloysite samples started, but it was not until the eleventh day that any change was observed in the nontronite. The effect

was a change of the interface material to a bright green from its original yellowish green.

The conditions of pH and Eh in the solutions above the clays (which had flocculated and were spread out on the bottom of the flask) at which bleaching occurred are shown on Fig. 1. These are:

	pH	Eh (V)
Kaolinite Y-3	5·5	+0·180
Halloysite 1-2	4·2	+0·220
Halloysite 6-2	5·3	+0·230
Nontronite H33a	5·75	+0·285

The conditions are therefore still oxidizing and within the stability field for hematite. The removal of ferric iron from the clay particles is a complex process

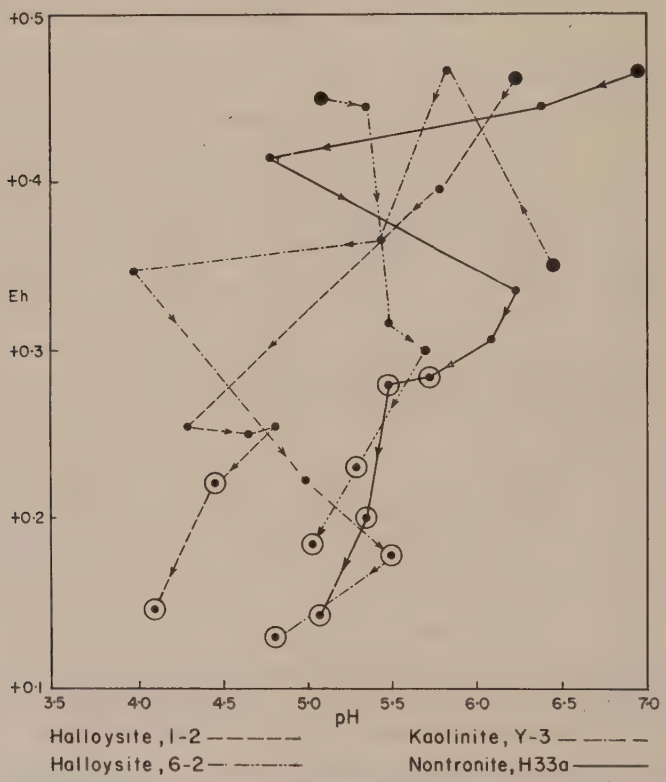

Fig. 1. Graph of Eh–pH in anaerobic bacterial cultures in fresh water with sucrose nutrient. Iron oxide films were removed from kaolinite and halloysite particles (<2 μ), and a change of colour took place in nontronite (crushed minus 0·053 mm). Dots represent daily readings, starting with the large dots at the top of the graph. The data are from Table 4. Circled dots are readings at which a change in the ferric oxide was observed visually. The circled dots for nontronite indicate the position at which a bright-green colour developed. Arrows indicate direction of change. Large dots are starting points.

which is due to a combination of several factors. STARKEY and HALVORSON (1927) and KRUMBEIN and GARRELS (1952) point out that the ferric–ferrous ratio is controlled by Eh and is determined by the equation:

$$\text{Eh} = E_0 + \frac{RT}{nF} \cdot \ln \frac{a_{Fe^{3+}}}{a_{Fe^{2+}}}$$

At 25°C for $n = 1$ the equations becomes:

$$\text{Eh} = E_0 + 0{\cdot}06 \log \frac{a_{Fe^{3+}}}{a_{Fe^{2+}}}$$

where R = gas constant, T = absolute temperature, n = number of electrons involved in the reactions, F = Faraday's constant, and a = activity.

Lowering the oxygen pressure, that is, creating more anaerobic conditions, will tend to increase Fe^{2+} at the expense of Fe (III) which is removed from the clay particles and goes into solution as Fe^{2+}. At the same time the pH is lowered. Reduction of both Eh and pH in this set of experiments is apparent from Table 4 and Fig. 1.

The production of carbon dioxide from the decomposition of sucrose by bacterial action results in a lowering of the pH and the production of glucose and dextrose. Glucose is a reducing and complexing agent and its presence changes the E_0 of the solution, which has an important bearing on the reduction of ferric to ferrous iron. In experiments reported by BLOOMFIELD (1950, p. 208) a mixed medium containing 1 per cent glucose was used; this is more concentrated than the sucrose medium (0·1 per cent) used in the experiments described here. In ALLISON and SCARSETH's (1942) method the clear supernatant containing ferrous iron in solution was drawn off periodically and the iron determined; this was done in the trial run of the present experiments, but in completely stagnant conditions the supernatant would remain and the conditions would be somewhat different. When the supernatant is removed, the iron in solution can be oxidized to ferric iron with hydrogen peroxide and the iron can be precipitated with ammonium hydroxide in the usual way. However, if the supernatant is not removed and bacterial fermentation is continued, an organic salt of iron is formed which is difficult to oxidize to obtain the ferric iron for precipitation with ammonium hydroxide. Ammonium hydroxide was used in preference to the more rapid colorimetric methods because for nontronite it was expected that alumina might be removed in preference to iron, which was found to be the case. Careful observation during precipitation of ferric hydroxide and alumina often reveals the presence of both, as alumina seems to precipitate slightly in advance of ferric hydroxide.

The relative ease with which the ferric iron was removed from the various clay minerals in these experiments was found to be:

Halloysite 6-2 > Kaolinite Y-3 > Halloysite 1-2

The variation is caused by the different mineralogical forms in which the oxides are present. In Table 3, goethite is shown to be present in greater quantity than hematite for kaolinite Y-3 and halloysite 1-2, whereas hematite is the principal

iron oxide in halloysite 6-2 where it is accompanied by some goethite and some indefinite iron oxide. As mentioned previously, Fripiat and Gastuche (1952) noted different degrees of crystallinity in the iron oxide films that they produced experimentally on kaolinite. Bloomfield (1950, p. 206) noted that the rates of removal of iron oxide differed in the clays that he studied.

The amount of iron oxide removed from the clay minerals in this experiment was:

Mineral	Fe_2O_3 removed (%)	Percentage of total Fe_2O_3 present removed
Kaolinite Y-3	3·4	22
Halloysite 1-2	4·5	32
Halloysite 6-2	8·2	62
Nontronite H33a	3·2	10

The effects of this experiment on nontronite are discussed in a later section.

Bacterial action in sea-water, aerobic conditions. The effect of sea-water inoculated with bacteria from the Great Bahama Bank on kaolinite Y-3, halloysite 1-2 and halloysite 6-2 was examined by an experiment similar to that described for fresh water. The sea-water was obtained through the courtesy of P. E. Cloud, Jr., of the U.S. Geological Survey, who collected it from the Gulf Stream in the Florida Straits. The bacteria were present in soft carbonate cores that were collected for a study of carbonate sedimentation. The bacteria grew in aerobic conditions at a temperature of 35°C; they showed no activity under anaerobic conditions at 25°C in the same sea-water and nutrient. As marine organic matter differs from that in soils, a nutrient solution was made of casein, yeast and a small quantity of sucrose in water. The experiment was continued for 21 days, by which time all the minerals showed a reduction of colour. The clays were originally redispersed in the sea-water, which was made up to 200 ml; 10 ml of nutrient was added at three separate times. The pH of the original sea-water was 7·95 and the Eh was +0·380 V. The variations in pH and Eh during the course of this experiment are shown in Table 5 and Fig. 2.

After an initial fall in pH from about 8 to 5 as the result of addition of clay minerals and nutrient, the pH gradually rose until at the end of the experiment it was near normal for sea-water (Table 5). The Eh, however, was lowered during the course of the experiment to the final readings of +0·055 to +0·085, which is just on the border of the stability field for hematite at this pH value (Krumbein and Garrels, 1952, Fig. 3, p. 15).

No attempt was made to analyse the supernatant because of the complex relationship of organic matter and sea-water which was believed to be present. The supernatant was foul smelling and appeared to be similar to that in stagnant beach pools where organic matter is present; it was brown in colour, in contrast to the colourless supernatant of experiment (1), and some part of the iron was in solution as indicated by the bleaching of the clay minerals. It was observed that halloysite 6-2 bleached more readily than either of the other two clays, as in the freshwater experiment.

Table 5. Conditions of pH and Eh in sea water inoculated with aerobic marine bacteria in contact with clay minerals*

	Anaerobic†						Aerobic			
Date	10 August 1956		11 August 1956		13 August 1956		14 August 1956		15 August 1956	
	pH	Eh	pH	Eh‡	pH	Eh	pH	Eh	pH	Eh
Kaolinite, Y-3	5·3	+0·385	5·50	+0·355	5·00	+0·335	5·52	+0·295	6·3	+0·180
Halloysite, 1-2	5·25	+0·380	5·20	+0·295	5·10	+0·230	5·27	+0·315	6·02	+0·230
Halloysite, 6-2	5·40	+0·365	5·65	+0·290	5·22	+0·235	5·50	+0·305	6·42	+0·185

	Aerobic									
Date	16 August 1956		17 August 1956		20 August 1956		21 August 1956		22 August 1956	
	pH	Eh	pH	Eh	pH	Eh	pH	Eh‡	pH	Eh
Kaolinite, Y-3	6·95	+0·245	7·22	+0·245	6·98	+0·180	7·18	+0·290	5·4	+0·080
Halloysite, 1-2	6·52	+0·155	6·95	+0·185	6·40	+0·175	6·79	+0·135	4·65	+0·215
Halloysite, 6-2	6·95	+0·205	7·15	+0·155	7·00	+0·150	7·40	+0·215	4·70	+0·130

	Aerobic					
Date	29 August 1956		30 August 1956		31 August 1956	
	pH	Eh	pH	Eh	pH	Eh
Kaolinite, Y-3	7·55	+0·210	7·50	+0·115	7·58	+0·080
Halloysite, 1-2	6·95	+0·170	7·0	+0·095	7·15	+0·085
Halloysite, 6-2	8·10	+0·185	8·08	+0·085	7·98	+0·055

* Protein-rich nutrient added, kept at 35°C. The bacteria used were from the Great Bahama Bank, and required aerobic conditions at 35°C for growth.

† The experiment was set up under anaerobic conditions, but the bacteria died; a change to aerobic conditions with a fresh inoculation was made on 14 August 1956.

‡ Additional nutrient added.

Bleaching of all three clays occurred on 30 August 1956.

Bacterial action in black mud, marine lagoon environment, anaerobic conditions. A stagnant marine lagoon environment, such as occurs on coasts with shallow inlets in which organic matter accumulates, was simulated by using a sample of black muck collected by J. C. Hathaway, U.S. Geological Survey, at Martha's Vineyard, Mass. This muck consisted of fine to coarse sand with much black organic matter and had a fetid odour of hydrogen sulphide. About $\frac{1}{4}$ lb of this muck was shaken up in sea-water and allowed to settle. When the supernatant was clear and free from sand, although it still contained some finely divided organic matter, some of it was removed and used in Erlenmeyer flasks with the same clay minerals as in the experiments described above. The quantities used in this experiment were: 1 g each of kaolinite Y-3, halloysite 1-2, and halloysite 6-2

and 0·5 g of nontronite H33a. These were dispersed in sea-water and 50 ml of the prepared supernatant containing sulphur bacteria added to the large samples and 20 ml added to the nontronite sample. A volume of 10 ml of casein-yeast nutrient was added to each and the flasks were stoppered as before and kept at 25°C. The supernatant had a pH of 7·25 and an Eh of −0·095 V. This Eh indicates conditions a little above the stability field for pyrite, but below that for hematite, that is, in the siderite field (KRUMBEIN and GARRELS, 1952, p. 12), presuming that other

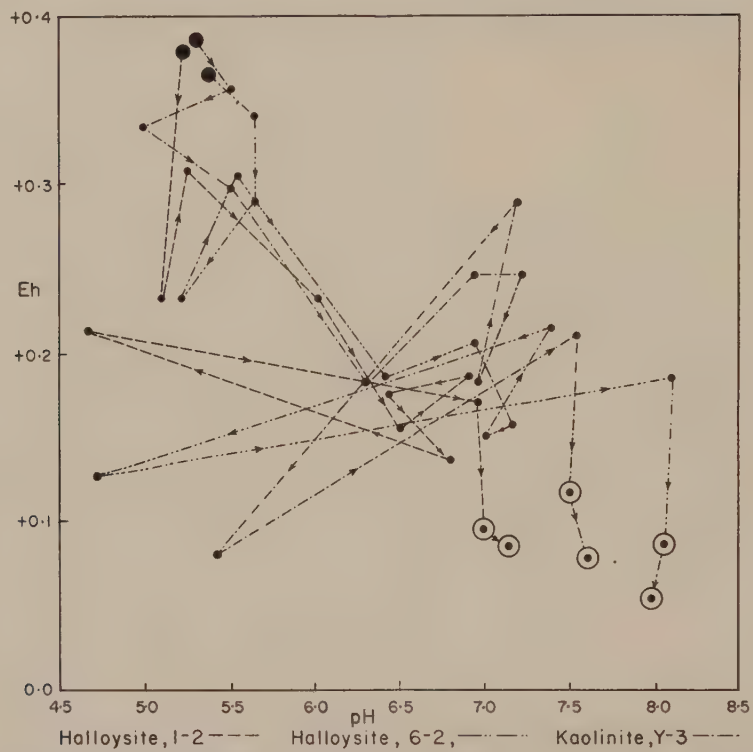

Fig. 2. Graph of relationship of Eh and pH in aerobic culture of marine bacteria from the Great Bahama Bank calcareous sediment. Data are plotted from the figures in Table 5. Iron oxide films showed bleaching at conditions indicated by circled dots. The initial pH and Eh of the sea-water culture were 7·95 and +0·380 V, respectively. Variations in Eh and pH are partly due to the addition of nutrient, but continued growth of bacteria produced the same final conditions with each clay mineral. Arrows indicate direction of change. Large dots are starting points.

conditions would produce such an environment. It was expected that hematite and other iron oxides would become unstable under these conditions, which approximate VAN STRAATEN's (1954) monosulphuric anaerobic zone. The changes in pH and Eh during the course of the experiment are given in Table 6 and illustrated in Fig. 3.

Immediately on addition of the prepared water the clays started to bleach and the nontronite turned greenish, as toward the end of the fresh-water experiment. On the first day the supernatants were brown after the clays had flocculated, but on the next day they became black and similar in appearance to the original

Table 6. Conditions of pH and Eh in a simulated stagnant marine lagoon-type environment*

Date	30 August 1956		31 August 1956		1 Sept. 1956		3 Sept. 1956		4 Sept. 1956		5 Sept. 1956	
	pH	Eh	pH	Eh	pH	Eh	pH	Eh	pH	Eh	pH	Eh
Kaolinite, Y-3	6·08	+0·175	6·40	−0·025	6·75	−0·050	6·70	−0·065	7·05	−0·055	6·85	−0·095
Halloysite, 1-2	5·95	+0·165	6·35	−0·015	6·70	−0·080	6·70	−0·095	7·60	−0·095	6·85	−0·105
Halloysite, 6-2	6·10	+0·175	6·45	−0·020	6·62	−0·085	6·70	−0·075	7·05	−0·070	6·80	−0·105
Nontronite, H33a	5·95	+0·050	6·20	−0·020	6·35	−0·065	6·40	−0·085	6·90	−0·075	6·65	−0·095

* Sea water inoculated with bacteria from black muck, protein nutrient, kept at 25°C.

muck. The experiment was allowed to continue for 12 days, by which time the original bacterial action had ceased and the supernatants were yellowish and rather dense in appearance. Possibly a little sulphur was being deposited.

Kaolinite Y-3 and nontronite H33a were removed from the supernatants by

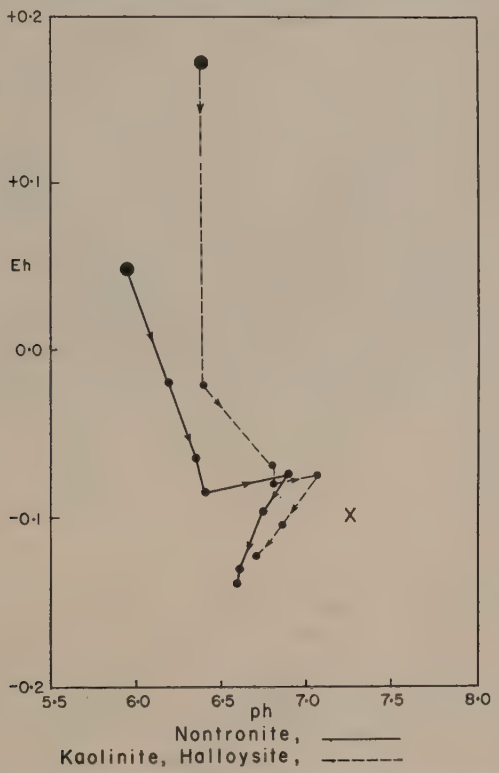

Fig. 3. Graph of relationship of Eh and pH in anaerobic marine lagoon black mud environment. Bacterial inoculation was obtained from black muck from Martha's Vineyard. The data are in Table 6; as the figures for kaolinite and the two samples of halloysite are very similar, they were averaged. The pH and Eh of the original solution before adding the clay samples is shown at *X* (pH 7·25, Eh −0·095). Dots represent daily readings, starting with the large dots. Arrows indicate direction of change.

centrifuging, washing in distilled water and then in 95 per cent alcohol, and allowing to dry. Both clays were intensely black, and an interesting feature was the presence of clumps or aggregates of uneven shape (Fig. 4) associated with colourless crystals of low birefringence. The clays were left exposed to the air for 48 h, by which time they had reverted to the oxidized condition. Kaolinite Y-3 was brown but

had lost its original reddish tones, implying that some iron had gone into solution. The nontronite was a slightly deeper shade than the original but was similar in colour and possibly also in FeO–content to that in another experiment to be described. The clumps in the clays broke down slightly on drying and may have been caused by the binding action of bacteria. Similar results were observed by van Straaten (1954, p. 38–45) with the muds from the Wadden Sea in Holland.

Removal of iron from within the clay mineral lattice

The nontronite used in these experiments (A.P.I. no. H33a) contains 29·46 per cent of Fe_2O_3 and 0·28 per cent of FeO. The ferric iron, and presumably also the small amount of ferrous iron, is in the octahedral layer with magnesium and some of the aluminium.

Table 7. Change in pH and Eh of sea-water after addition of ferrous nontronite*

Date	pH	Eh	Remarks
21 August 1956	7·95	+0·380	Sea-water before addition of nontronite
22 August 1956	6·72	+0·315	Nontronite bright green
23 August 1956	7·25	+0·317	Nontronite changing to brown
24 August 1956	7·29	+0·384	Nontronite with brown flocculant appearance
27 August 1956	7·37	+0·424	Nontronite practically all changed to the brown flocculant material
28 August 1956	7·44	+0·405	
29 August 1956	7·68	+0·290	
30 August 1956	7·55	+0·195	
31 August 1956	7·51	+0·155	

* About 0·25 g nontronite in 50 ml sea-water.

Reducing conditions produced by bacteria in fresh water (described above) caused the nontronite to turn bright green in colour, the whole sample superficially resembling glauconite in appearance. The whole sample had turned green 17 days after the experiment had started when the conditions were: pH 5·12 and Eh +0·143 V. The green colour persisted at Eh +0·235 V, at which time the mineral was removed. An X-ray diffraction pattern made by J. C. Hathaway of the U.S. Geological Survey showed that there was no change in the lattice structure. On exposure to the air the green colour faded but the FeO content had increased to 1·7 per cent (analysed by Katrine White, U.S. Geological Survey). The mineral is subsequently referred to as ferrous nontronite. It decomposed very rapidly in concentrated HCl, leaving amorphous silica.

A small quantity of ferrous nontronite was placed in sea-water (pH 7·95, Eh +0·380) and left for 18 hr, by which time the mineral had turned brown at the interface with the sea-water, indicating oxidation of ferrous to ferric iron. There was also a brown scum of ferric hydroxide on the surface of the water and on the sides of the beaker. The changes in pH and Eh of the sea-water on the addition of the nontronite are given in Table 7.

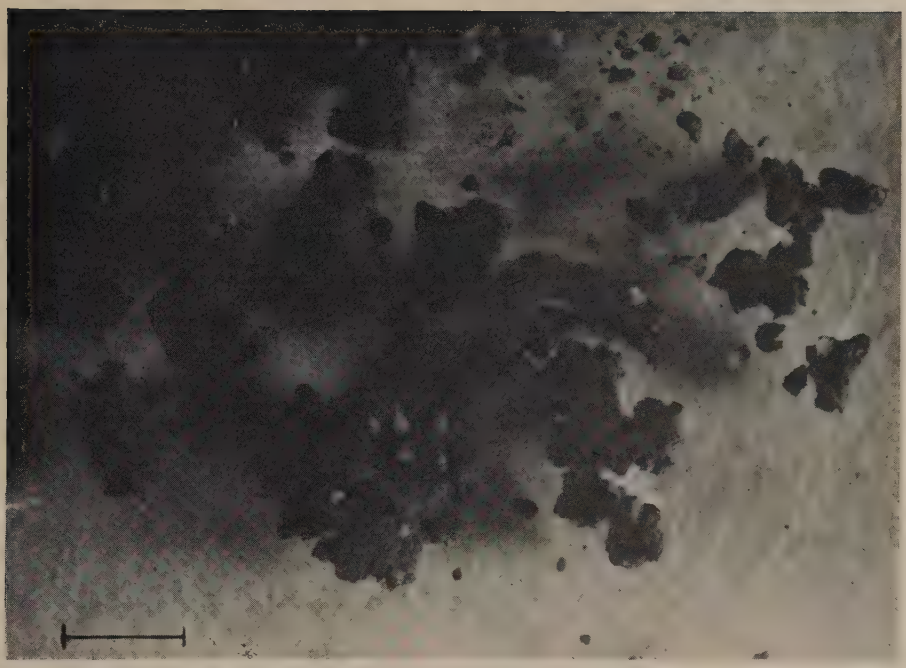

Fig. 4. Black aggregates of kaolinite Y-3 formed as a result of bacterial action in a marine lagoon black mud environment with sulphur bacteria. This granular texture is stated by HARDER (1919, p. 84) to be characteristic of ferrous sulphide deposits. Scale represents 1 mm. Photo by H. C. STARKEY.

The effect of ferrous nontronite is to reduce the Eh of sea-water by the addition of Fe^{2+}, which changes the Fe^{3+}/Fe^{2+} ratio. Simultaneously the pH is lowered slightly.

The nontronite had turned completely brown by the end of the eleventh day. It was then removed, washed with distilled water, and dried at room temperature. An X-ray diffraction pattern showed that it still retained the montmorillonite structure.

Effect of Sea-Water on Clay Minerals

In normal sea-water with oxidizing conditions the effect on clay minerals such as montmorillonites, especially nontronite, is principally in the exchange relationships; ferrous iron present will be oxidized to ferric iron, and if this reaction occurs the pH and Eh of the sea-water will be altered. Therefore the addition of clay minerals to sea-water effects a change in the sea-water itself; the greater the quantity of clay added, the greater this change will be. After a time interval, an equilibrium state will be established fairly rapidly, judging by the results from the experiments described.

Stability of the clay mineral structure

The stability of the clay minerals in certain environments as defined by the pH and other factors is implied in Table 2. The change from one environment to another may cause instability of the crystal lattice. This can take place in two stages: (1) replacement of the original exchangeable cations by others present in the new environment; and (2) removal of parts of the crystal lattice, either the octahedral or the tetrahedral layer.

The principal natural causes will be the alteration of the mineral lattices by removal from an environment in which the mineral is stable to one in which it may not be stable, i.e. deposition of montmorillonite in an environment with low pH, or transportation and deposition to a marine environment, or conversely, the changing of the character of the ground-water or soil-water or both if the clay mineral remains *in situ*. Such a change would be, for example, the flooding of soils by salt water as in the inundation during World War II near the Zuyder Zee in Holland; or conversely, the reclamation by which marine marshes are changed into arable land. Another example is the removal of soils from the latest alluvium of a stream to a terrace in which the pH is changed from 7–8 to 4–5 as in some of the older terraces in the vicinity of Middle River, Augusta County, Virginia. Leaching of the carbonates from soils in glacial moraines in the northern parts of the United States is a change of environment for the clay minerals in such soils.

In the deposition of sedimentary materials in marine situations the sea-water will have an effect on the clay minerals present, and conversely the clay minerals will affect the sea-water with respect to pH and Eh; in addition, the removal of Mg, Ca, K, and Na from sea-water to exchange positions will vary the composition of the sea-water.

A number of clay minerals were placed in sea-water and in a 3·5 per cent NaCl solution for a period of 10 days. The loss in weight and change in ion-exchange capacity are shown in Table 8.

Table 8. Loss of weight and change in ion-exchange capacity of clay minerals after soaking in 3·5 per cent NaCl solution and in sea-water for 10 days

	Loss in weight (%)		Ion-exchange capacity, meq/100 g		
	3·5 per cent NaCl Soln.	Sea-water	Original	3·5 per cent NaCl Soln.	Sea-water
Montmorillonite	53·5	6·0	89·0	62·4	87·2
Metabentonite	22·0	5·0	23·0	27·1	35·1
"Illite"	13·7	6·7	21·0	14·9	16·0
Kaolinite	1·9	1·8	3·4	1·7	3·3
Halloysite	5·8	3·3	11·0	6·4	10·8
Kaolinite Y-3	10·9	1·7	17·2	9·0	15·3
Halloysite 1-2	4·0	4·3	15·0	18·0	24·2
Halloysite 6-2	4·4	4·3	21·4	51·1	22·4

With these treatments kaolinite is the most stable mineral in sea-water, followed by halloysite, metabentonite, montmorillonite, and "illite." (No chlorite was available for examination). In NaCl solution most of the minerals were less stable with the exception of kaolinite and halloysite. The kaolinite with better crystallinity is more stable in NaCl solution than kaolinite Y-3 with poor crystallinity. It is probable that the magnesium ions in sea water have a stabilizing effect on the crystal lattice so far as montmorillonite, metabentonite and "illite" are concerned, whereas the absence or presence of additional ions in sea water has little effect on kaolinite and halloysite because of the different nature of the exchange reaction. The NaCl solution used here had a pH of 6·10 so that the solution has acted as a slightly acid one rather than as one that can supply ions for exchange positions. The results for sea-water substantiate the findings of GRIM and JOHNS (1954) for montmorillonite, but they also point to the fact that kaolinite will remain stable, that is, the structure will not break down, for longer periods of time than they have suggested.

Exchange capacity of clay minerals soaked in sea-water

In sea water most of the minerals have exchange capacities comparable with those taken at pH 7 in the usual procedure; metabentonite shows an increase comparable with that in NaOH. Only one of the halloysites, 1–2, shows an increase, and the kaolinites have exchange capacities similar to those for the untreated minerals. Montmorillonite has practically no loss in exchange capacity, a fact noted by KELLEY and LIEBIG (1934), who examined the exchangeable cations of a soil and of a bentonitic clay from Otay, California, after treatment with sea-water. Their results are shown in Table 9.

The bentonitic clay was altered by the sea-water much more than was the soil, but both exchangeable Mg and Na were increased at the expense of Ca in the soil, and, in the bentonite, Mg, K, and Na were all increased, the Mg to nearly half the total exchangeable ions. The molecular ratios of the dissolved cations in sea-water are : K, 1·0; Ca, 2·5; Mg, 11·5; and Na, 49·5, so that sea-water contains about 4·3 eq of Na to one of Mg, but the greater replacing power of Mg is responsible for

Table 9. The exchangeable cations of a soil and of a bentonitic clay from Otay, California, after treatment with sea-water (KELLEY and LIEBIG, 1934).

	Exchangeable cations (meq/100 g)			
	Ca	Mg	K	Na
Soil, before treatment*	21·7	6·0	1·36	1·22
Soil, after treatment	6·0	11·0	1·98	10·12
Bentonite, before treatment	106	—	—	—
Bentonite, after treatment	10·8	48·3	6·9	39·1

* Treatment consisted of leaching with $CaCl_2$ to produce a calcium clay, which was shaken with a considerable volume of sea-water and then leached with sea-water for several days, after which the exchangeable cations were determined.

the extra Mg in a mineral such as montmorillonite. Exchange reactions are probably responsible for the greater stability of montmorillonite in sea-water than in a 3·5 per cent solution of NaCl, which is of comparable strength to that of sea-water (see Table 3). HENDRICKS and ROSS (1941) in their study of glauconite genesis also noted the influence of Mg in the glauconite lattice and pointed out that Mg is on the average 0·32 ion with a range of 0·26–0·52 ion in thirty-two analyses of glauconite. This reflects the requirements of the mineral lattice and the stability of the environment.

Minerals such as montmorillonite with interlayer water and unsatisfied negative charge due to isomorphous substitution within the octahedral or tetrahedral layer or both are much more susceptible to change than those with a structure like kaolinite where the internal charges are satisfied and broken bonds at the edges provide the sites for exchange reactions. Disorder and randomness in the stacking of the layers here increase both the exchange capacity and the ability to break down with change of environment.

MUKHERJEE *et al.* (1947; 1948) have shown that Fe, Al, and Si ions are released from clay minerals after treatment with 0·02 N HCl and then saturation with a salt solution ($BaCl_2$). In part this may be due to the induced acidity (the H-form is produced) whereby such ions are dissolved from the surfaces of the clay minerals, particularly where there are coatings of iron oxide. It is unlikely that this is an exchange reaction, for exchangeable Fe is not common, so far as is known, nor are exchangeable Al or Si, although exchangeable Al does occur. In one of the experiments described in this paper, Al was released from nontronite when the solution in which it was placed became acid, and later a small quantity of Fe was released, presumably from the mineral lattice. Repeated change to the H-form and leaching with a salt probably caused a breakdown of the mineral structure in MUKHERJEE's experiments (MUKHERJEE *et al.*, 1947; 1948). MUKHERJEE reports that montmorillonite is much less stable than kaolinite. Thus it is suggested that if rivers transport clay minerals in the H-form the effect of sea-water may be greater on them than if they have a variety of exchangeable ions present.

Effect of sea water containing hydrogen sulphide on clay minerals

The effect of sea-water containing hydrogen sulphide, in an amount comparable to that reported from the bottom of the Norwegian fiords by STRØM (1939), on

kaolinite, halloysite and nontronite is given in Table 10 and illustrated in Fig. 5. The sea-water had 40 ml/l of hydrogen sulphide slowly bubbled into it from a cylinder to which a gauge was attached for measuring purposes. It is assumed that all the hydrogen sulphide added was dissolved in the water, as the amount

Table 10. Relation between pH and Eh in sea-water, containing hydrogen sulphide,* in contact with clay minerals

Date	20 August 1956		21 August 1956		22 August 1956		29 August 1956	
	pH	Eh	pH	Eh	pH	Eh	pH	Eh
Kaolinite Y-3	7·32	+0·200	6·85	+0·290	6·70	+0·315	6·60	+0·245
Halloysite 1-2	6·90	+0·205	6·85	+0·305	6·82	+0·320	6·80	+0·260
Halloysite 6-2	7·05	+0·195	6·50	+0·307	6·55	+0·327	6·60	+0·275
Nontronite, H33a	6·63	+0·196	7·25	+0·315	7·20	+0·335	7·12	+0·285

* 40 ml H_2S/l.; initial pH, 7·0; Eh, −0·025.

was less than one-tenth its solubility in water. The resulting pH was 7·0 and the Eh −0·025 V. When the clays were added to the flasks, air was excluded by rubber stoppers, but there was no rubber tube to allow the gas to escape.

When nontronite was first shaken up with this sea-water it turned bright

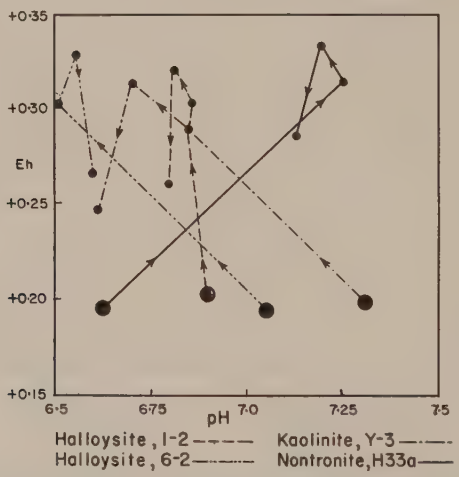

Fig. 5. The effect of clay minerals on sea-water containing 40 ml H_2S/l.; data from Table 8. The initial pH and Eh of the sea-water were 7·0 and −0·025 V, respectively. Arrows indicate the direction in which changes took place during a period of 9 days as the clay minerals were coming to equilibrium in the sea-water. The oxidizing effect of the iron oxide films has raised the Eh but there is little change in pH. The large dots indicate starting points.

green; the next day green spots still persisted in the nontronite on the bottom of the flask, but these disappeared when the flask was shaken, and the mineral became adjusted to its environment. No change was observed in the colour of the other clay minerals, but it is assumed that they had an oxidizing effect which resulted in nearly normal readings for sea-water, that is, +0·380 V (on 22 August

1956), but 7 days later the Eh had fallen to an average of +0·266 V. Although additional experiments are required, it is felt that the changes in Eh are not due to oxidation in air while the readings were made. The Eh–pH relationship is shown in Fig. 5. The results of these experiments indicate the effects that can take place on the interface between the ocean floor and the ocean water.

Discussion

Effect of marine environment on iron oxides associated with clay minerals

The kinds of clay minerals transported to a marine environment will depend, as Grim (1951, p. 229) has pointed out, on those present in the area. Iron oxides, if present as films on the clay mineral micelles, will be carried along with the clay minerals, and if conditions of pH and Eh do not change the iron oxides will be incorporated in the resulting sediments. The experiments described here indicate the course of events that may take place after deposition in a marine environment. Several possibilities are to be considered:

Iron oxide films are not removed from clay particle surfaces. Red, brown or yellow sediments indicate the presence of ferric oxides, hematite, goethite or indefinite iron oxides which are stable in sea-water with Eh +0·1 to 0·3 (Krumbein and Garrels, 1952, p. 3) at the bottom; that is, oxidizing. It should be noted that although both Eh and pH measure the solubility of ferric oxide, there is a very narrow range in pH for normal sea-water, so that the relationship to pH is not nearly so important as that to Eh. Sea-water alone will not dissociate ferric oxides from clay minerals, as the Eh is similar to that for many soils in which iron oxide films and coatings are formed. Some loss of weight in the minerals may occur (Table 10). Exchangeable ions are important in all clay minerals except kaolinite and halloysite, in which the total exchange capacity is practically unchanged from its original quantity, although the exchangeable cations may be present in different proportions.

Iron oxide films are removed from clay particle surfaces. The stability field for the existence of solid ferric oxide and ferrous oxide is governed by the oxidation–reduction potential present according to the equation (Castano and Garrels, 1950, p. 757):

$$\mathrm{Eh} = +0{\cdot}06 \log \frac{a\mathrm{Fe}^{3+}}{a\mathrm{Fe}^{3+}}$$

Lowering Eh (conditions become more anaerobic) will increase Fe^{2+} at the expense of Fe^{3+} and at the same time decrease the pH (Starkey and Halvorson, 1927, p. 382). Conversely, raising the Eh (conditions become more aerobic) will increase the amount of Fe^{3+} at the expense of Fe^{2+}. Ferrous ions will be in solution, probably in equilibrium with $Fe(OH)_2$ at low Eh values, but if the Eh is raised, Fe^{2+} changes to $Fe_2(OH)_3$, which will precipitate if the amount exceeds the solubility in sea-water. Cooper (1938, Table VI) has summarized the activities of Fe^{3+} and Fe^{2+} in equilibrium with sea-water containing solid ferric hydroxide.

The fluctuation between oxidizing and reducing ions will determine the quantities of Fe^{3+} and Fe^{2+} present. There are two important environments: the interface between the sea-water and the ocean floor; and the sediments below the

ocean floor. These have been illustrated by Krumbein and Garrels (1952, p. 20) and Huber and Garrels (1953). Several environments may now be examined:

Marine environments and their influence on iron oxides associated with clay minerals

Unrestricted marine environment with little or no bacterial activity. The sea-floor interface in an unrestricted sea subject to circulation of water will have pH and Eh similar to that of ordinary sea-water; e.g. pH 7–8, Eh +0·1–0·3 V. Under these conditions iron oxide films will be stable on the clay particles and no removal will take place. The resulting sediments will be similar in colour to those being transported by the rivers to the area. Some adjustment of crystal lattices may take place with time. Exchangeable cations will be readjusted to those of the marine environment. It is supposed that in this environment the addition of organic matter is at a minimum and that bacterial activity is not marked.

Shallow marine environment with little or no bacterial activity. In such an environment bacterial activity will reduce the Eh, but the pH remains approximately the same as in normal sea-water. This is an environment similar to that of the experiment with sea-water and Bahama Bank bacteria. As the Eh is lowered, ferric iron becomes unstable and is removed with consequent bleaching of the clay particles. Below the interface, bacterial activity may increase but will depend on the availability of organic matter for growth of the bacteria. This environment could well occur on wide shallow estuaries with little movement of water; it is aerobic in that some circulation of water occurs.

Restricted shallow water, marine environment with bacterial activity. The abundance of organic matter and bacteria results in strongly reducing conditions, as in stagnant water inside offshore bars. The experiment with inoculant from Martha's Vineyard was designed to examine this type of environment. The Eh is sufficiently low for reduction of ferric oxide to ferrous oxide, which is unstable and will change to Fe_3O, but in addition the presence of sulphides causes deposition of uncrystallized $FeS{\cdot}nH_2O$, and if sufficient time elapses pyrite and possibly marcasite develop. Edwards and Baker (1951) have observed that pyrite forms in marine muds that have an alkaline or neutral reaction. Ferric oxide in clay mineral lattices is changed to ferrous. A feature of this type of deposit is that the iron is not removed but remains in its new form associated with the clay minerals except for a small quantity that has crystallized as pyrite. At the interface where the Eh is higher, oxidation occurs and the black clay changes to brown. If the whole surface is exposed, oxidation similarly takes place and goethite and hematite, probably with indefinite iron oxides, result. Such situations have been described for Wadden Sea in Holland, and similar conditions are found in many near-shore areas.

The results of the fresh-water experiment indicate that at the interface of the floor of a fresh-water lake containing clay-bearing sediments, ferric iron can be reduced to ferrous iron if bacterial activity takes place. It should be noted, however, that pH is a limiting factor for bacterial growth. The iron removed from the surfaces of the clay particles is in the ferrous form and later forms a ferrous organic salt. The organic salt may be one method of transporting iron in solution.

The chamosite environment. One of the difficulties of explaining the large

quantities of chamosite that occur in such formations as the Northampton sand ironstone has been the lack of sufficient iron solution in sea water. Taylor (1949, p. 80) has discussed the various theories of transportation of iron into the basin in which the Northampton sand ironstone was formed. The association of chamosite with siderite indicates a definite environment limited by a pH of 7·0 to 8·0 and Eh of +0·05 to −0·10 V, but probably mainly below the zero Eh line (organic matter fence) as shown by Krumbein and Garrels (1952, Fig. 8, p. 26). In this field chamosite and siderite coexist; the presence of a small quantity of pyrite indicates the lower part of this field. Hallimond (1925, p. 98) regards chamosite as a result of the interaction of clay and ferrous iron. The clay derived from the weathering and erosion of land surface can carry with it sufficient iron to provide the iron in the chamosite which has subsequently developed in a shallow marine environment. For example, the kaolinite (fraction $<2\ \mu$) used in the experiments described in this paper has 15 per cent free iron oxide attached to the outside of the particles. This is equal to 336 lb ferric oxide in 13 ft^3 (1 ton) or in 52 ft^3 of soil, assuming that the soil contains 25 per cent clay. In the experiment with bacteria in sea-water ferric iron was changed to ferrous at +0·055, which is just on the lower edge of the stability field for hematite. Further evidence is provided by the ironstone mineralogy. The presence of both siderite and pyrite indicates that probably the condition under which the change from ferric to ferrous took place was more nearly like that of black mud with much bacterial activity to keep the Eh low. Experiments with fresh water and with a black sulphide inoculant show that in minerals such as nontronite the ferric iron will change to ferrous iron in conditions with a higher Eh in the presence of organic acids. Kaolinite present in the ironstones may be evidence that this mineral acted as a carrier of iron and that it is residual; further evidence is the fact that the chamosite is the kaolinitic type (Brindley, 1951, p. 520), the structure being a disordered one such as is very often found in soil clays. Further information given by Youell (1955) indicates that there is a range in the disorder of the chamosite lattice. Another piece of evidence suggested by Taylor (1949, p. 80) is that the climate of the land surrounding the depositional basin was warm and humid with abundant vegetation. Such a climate at the present time would have deep reddish-brown to red kaolinitic or halloysitic soils with abundant ferric oxide films on the clay particles and would be similar to those described by Fripiat and Gastuche (1952) or by Mohr and van Baren (1954).

The glauconite environment. Hendricks and Ross (1941) have reviewed the literature on glauconite formation. Glauconite has formed from muds—its immediate parent material—that are associated with decaying organic matter and pyrite or marcasite, or both. This observed association brings glauconite into the same stability field as chamosite, but rather lower than the position shown by Krumbein and Garrels (1952, Fig. 3, p. 26) because of the very common association with pyrite. The pH will be between 7·0 and 8·0 and the Eh near −0·20 V. The constancy of the magnesium content in glauconites from many localities is an important indicator of uniformity of environment (sea-water). It was noted in an earlier section of this paper that soaking of montmorillonite in sea water causes a rearrangement of the proportions of the exchangeable cations as reported

by Kelley and Liebig (1934). Hendricks and Ross (1941) reported a similar increase in magnesium in a montmorillonite that had developed from volcanic ash in a marine environment. It is suspected that for hydrous mica a similar rearrangement may also take place.

The shallow-water marine environment with restricted circulation and abundant organic matter for bacterial activity, similar to that described in the experiment, could very well be the natural habitat for glauconite formation. The clay minerals entering such an environment from land masses in temperate climates would be hydrous mica and degraded chloritic and vermiculitic minerals rather than kaolinite or halloysite. The Wadden Sea clays, for example, consist of 80 per cent or more of hydrous mica (Favejee, 1951, p. 140). Both ferric and ferrous iron are present in the octahedral layer of glauconite. Experiments with nontronite have shown that under reducing conditions part of the ferric iron will change to the ferrous state. In nontronite allowed to remain only a short time in reducing conditions, most of the ferrous iron reverts back to the ferric state when the mineral is placed in oxidizing conditions, but less reversion may occur if the reducing conditions continue for long periods of time, i.e. the clay mineral lattice may become stable in its environment. The weathering product of both chamosite (Taylor, 1949, p. 53) and glauconite (Cole, 1941, p. 242) is a ferric oxide which has been referred to as limonite, but the change to limonite is a very slow one. This suggests that beds of chamosite and of glauconite have been under reducing conditions for very long periods of time; during that time reducing conditions must have been maintained by bacterial action because sea-water is oxidizing, and mineralogical changes would take place. The non-removal of iron from these environments is probably due to several factors, among which are: reducing conditions maintain the iron in a ferrous condition which is nevertheless still closely associated with the clay mineral to which it was originally attached, either as a film of ferric oxide or as a part of the mineral lattice as in nontronite; slow sedimentation of new material would not change conditions from reducing to oxidizing; low solubility of ferrous and ferric hydroxide in sea-water would prevent removal of iron from its site of deposition. The total quantity of iron in true solution in sea-water after equilibrium has been obtained is not more than 4×10^{-7} mg Fe/m^3 at pH 8·0 (Cooper, 1938, p. 306). Ferrous hydroxide is soluble to $10^{-2.7}$ moles/l. at the same pH.

In many publications the importance of iron-reducing or sulphate-reducing bacteria has been discussed, and it is true that such bacteria do have important effects on the precipitation of ferric hydroxide or of iron sulphides. However, the effect of both aerobic and anaerobic bacteria of many kinds is to produce reducing conditions in the cultures, and presumably also in the natural environments in which they grow (Hewitt, 1950, p. 98 *et seq.*). The reduction (lowering of Eh) is caused by the metabolism of the bacteria, which requires the oxidation of the nutrient material available to produce energy for growth. Each type of bacterium will have optimum pH conditions for growth. The range of Eh produced by the activities of aerobic bacteria is about +0·4 to −0·2 V; that for the anaerobic bacteria is about +0·5 to −0·4 V (Hewitt, 1950, p. 117). The nutrient material in cultures or in natural environments causes variations in the Eh conditions. Hewitt

(1950, p. 120) discusses the effect of glucose, which is often used in bacterial cultures and has a reducing effect that alone would be sufficient to reduce Fe^{3+} to Fe^{2+} without any bacterial activity; it therefore should not be used in experiments with ferric iron without due recognition of its reducing capacity.

Experiments in the bacterial reduction of iron should be interpreted with caution; the reduction is a side-effect of the growth of the bacteria and not a consequence of any particular species of bacteria.

Theil (1927) noted that bacteria, through their metabolic processes, can also affect clay minerals by causing solubility of alumina and silica. He found that five times as much alumina was removed by solutions in which bacteria were actively growing as by sterile solutions. In the experiments described here, alumina was removed from nontronite in a similar manner.

Conclusions

The association of iron with clay minerals is an important means whereby iron is transported by rivers to a site of deposition either in freshwater lakes or in marine environments. The free iron oxide films on minerals such as kaolinite and halloysite account for the addition of considerable quantities of ferric oxide to a sedimentary basin, and the iron content of clay minerals in which iron has a position in the lattice also contributes. The free iron oxide films can be removed by lowering the redox potential through the metabolic processes of bacterial growth in culture media supplied with nutrients. In natural environments the nutrients are supplied by organic matter growing and decaying *in situ* or transported into the sedimentation area.

Reducing conditions influence ferric iron in the lattice of nontronite, changing it partly to the ferrous form; on return to oxidizing conditions the ferrous iron changes back to the ferric state though the reversion may not be complete. Reduction and oxidation may be an important means of clay mineral change in such minerals as montmorillonite and hydrous micas. Sea-water causes a change in the proportion of exchangeable cations in montmorillonite and may well do so in other clay minerals.

Iron oxide films on clay particles as well as iron within the lattices form the source of much of the iron deposited as amorphous ferrous sulphide in restricted marine environments in which black muds develop. Black ferrous oxide may accompany the amorphous ferrous sulphide; the black material remains attached to the clay mineral particles and reverts to ferric oxide if the Eh is raised. This was observed in the laboratory but also occurs in natural situations if black muds of this type are exposed to the air.

Bacterial activity seems to be necessary to maintain reducing environments such as those in which chamosite and glauconite are believed to form; also in this category are the iron sulphides that occur as thin layers in shales like the Kupferschiefer, as suggested by Edwards (1956, p. 106).

The experiments described here suggest a number of points that should be investigated. Among these are: changes in the proportion of exchangeable cations in various clay minerals soaked in sea-water; solubility of clay minerals in sea-water with varying redox potentials; influence of structure on stability in sea-water; removal of silica and alumina from clay minerals soaked in sea-water for

varying periods of time; effects of any of these treatments on the structure of the clay mineral lattices.

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Paragenesis of sodium, potassium and uranium in volcanic rocks of Lassen Volcanic National Park, California

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Abstract—Statistical correlations between Na_2O, K_2O and U in volcanic rocks at Lassen Park, California (by the data published J. A. S. Adams) confirmed that the concentration of uranium in investigated rocks is not correlated geochemically with the process of fractional differentiation but is regulated by the migrations of uranium through the magmatic basin and its detention by the medium enriched with potassium.

In one of the previous issues of this Journal, valuable data on geochemistry of uranium were published (Adams, 1955).

Adams' solution has been analysed by the author with the aid of mathematical statistics, and the results acquired are somewhat different from those of Adams.

Below we give the results obtained by statistical analysis of Adams' data on Na_2O, K_2O and U. The novelty of statistical methods for the solution of geochemical problems made it advisable to give this paper a methodical orientation, with a fairly detailed description of the calculating techniques.

Table 1, borrowed from Adams' paper with the addition of column (6), gives the percentages of Na_2O, K_2O and U (in p.p.m.) in investigated andesite and dacite. Graphs in Fig. 1 illustrate a correlation between Na_2O and U, and K_2O and U. These graphs suggest an idea of linear correlation between investigated components.

To check this impression we calculated the correlation coefficients (r) for pairs of components, i.e. (Na_2O, U), (K_2O, U) and (Na_2O, K_2O). With this aim in view we availed ourselves of some of the methods used in mineralogy and petrography in the last 10 years (Vistelius, 1947, 1948, 1956).

In Table 2 an example of calculations of r for a pair Na_2O—U is given. As is known theoretically (Hald, 1952) and confirmed by geochemical practice (Vistelius, 1956), a significant coefficient of correlation (r) based on 19 observations must have $t \geqslant 3$ for responsible conclusions (and for routine conclusions $t \geqslant 2$). Here

$$t = \frac{z}{\sigma_z} \qquad (1)$$

where

$$z = \tfrac{1}{2}\, ln \frac{1 + r}{1 - r}$$

and

$$\sigma_z = \frac{1}{\sqrt{n - 3}}$$

n = number of observations, and z is taken from special tables (Hald, 1952).

Table 1. Contents of Na_2O, K_2O and U in rocks from Lassen Volcanic National Park, California (ADAMS)

Sample number	Rock description	% Na_2O	% K_2O	Average U (p.p.m.)	Calculated by (2) average U (p.p.m. (U'))
36	Raker Peak pyroxene andesite	3·26	1·26	1·0	0·9
35	Andesite	3·83	1·76	1·3	1·5
37	Twin Lakes andesite	4·13	1·44	1·4	1·1
7	1915 lava with pumice	4·36	1·89	1·6	1·7
17	Flatiron andesite	3·88	1·93	1·7	1·7
18	Pilot Mountain andesite	3·70	1·95	1·8	1·7
15	Table Mountain basalt	3·81	2·05	1·9	1·9
8	Raker Peak dacite	3·80	2·15	2·0	2·0
12	1915 dacite	4·29	2·39	2·1	2·3
13	1915 mud flow	4·27	2·52	2·1	2·4
10	Raker Peak dacite	4·29	2·16	2·2	2·0
16	Chaos ambles dacite	4·32	2·53	2·2	2·4
34	Dacite tuff	4·53	2·80	2·5	2·8
11	Raker Peak dacite	4·80	2·65	2·6	2·6
14	Chaos Crags dacite	4·54	2·99	3·0	3·0
5	Manzanita dacite	4·73	2·91	3·1	2·9
33	Dacite pumice	4·43	3·11	3·2	3·1
6	Pre-Lassen dacite	4·58	2·95	3·2	3·0
9	Raker Peak dacite	4·30	3·34	3·6	3·4

The calculated correlation coefficients (r) and the tests of their significance (t) are given below:

	Na_2O—U	K_2O—U	Na_2O—K_2O
r	+0·74	+0·97	+0·76
t	3·8	8·4	4·0

The obtained values of r and t indicate a strong correlation in pairs of components, i.e. Na_2O—U, K_2O—U and Na_2O—K_2O. Besides, the quantity of uranium can be calculated by the quantity of Na_2O and K_2O, as is shown in Fig. 1. An undoubted correlation between Na_2O and U, and K_2O and U may be used for calculation of the quantity of uranium in rocks by means of the quantity of Na_2O and K_2O. Necessary calculations are given in Table 3. As a result of the above calculations we have the equation

$$U = 1{\cdot}208K_2O + 0{\cdot}004Na_2O - 0{\cdot}627 \qquad (2)$$

with the aid of which we calculated the quantity of uranium in ADAMS' rocks collection in Table 1.

We proved a significant correlation between uranium and potassium and separately between uranium and sodium. This correlation is significant for the investigated rocks, but we have found no confirmation of this significance from a genetic and geochemical point of view. The fact is that we have three components

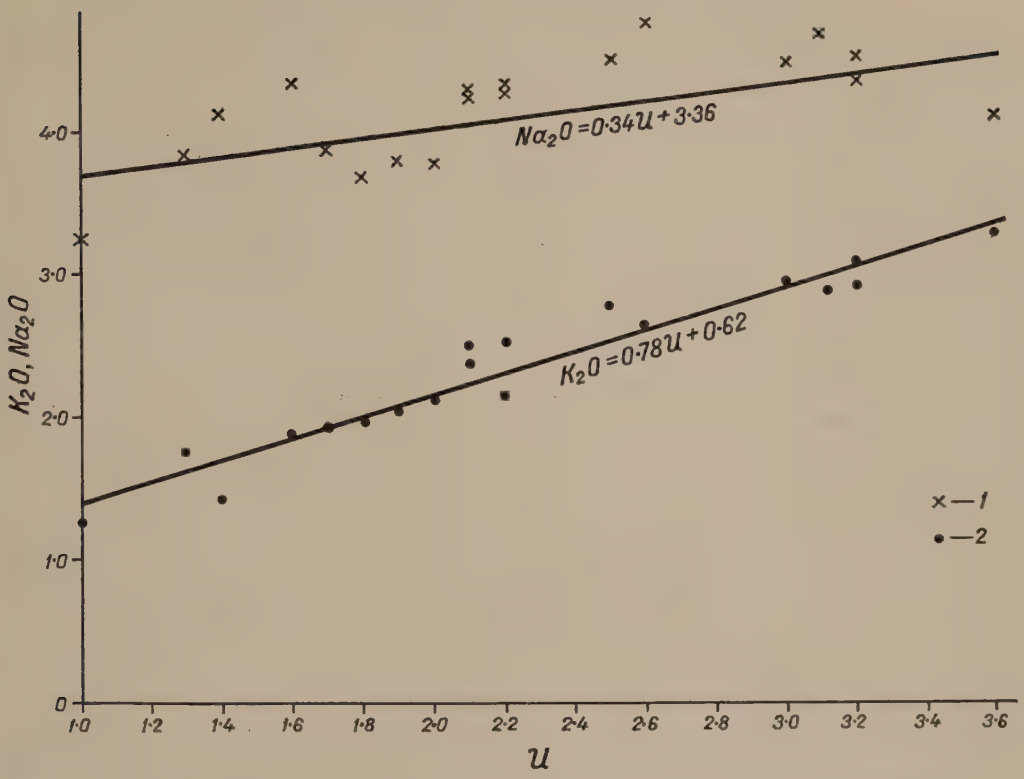

Fig. 1. Interrelations between Na_2O and U, and K_2O and U. 1—Na_2O, 2—K_2O. Straight lines—regressions Na_2O on U and K_2O on U (calculated from ADAMS' data).

with a strong correlation between every pair of them. Besides these is a possibility of uranium being correlated only with one component and the correlation of this component with the third leads to a false correlation between the first and the third components. For instance, A is correlated with B, B is correlated with C, consequently we have a correlation between A and C independent of natural sense of this correlation. Such situations were frequently observed in our previous mineralogical (VITELIUS 1948, 1954) and geochemical (VISTELIUS and ZOULFUGARLY, 1952) investigations.

To solve the question, we must calculate coefficients of partial correlation $\rho_{i,j.k}$. Partial correlation coefficients $\rho_{i,j.k}$ lead to the estimation of a linear correlation between i and j with constant values of k. In our case we must calculate $\rho_{Na_2O,U\cdot K_2O}$, $\rho_{K_2O,U\cdot Na_2O}$ and $\rho_{K_2O,Na_2O\cdot U}$ by using

$$\rho_{i,j.k} = \frac{r_{ij} - r_{ik} \cdot r_{jk}}{\sqrt{[(1 - r^2_{ik})(1 - r^2_{jk})]}} \qquad (3)$$

By (3) we obtain

$$\rho_{Na_2O,U\cdot K_2O} = +0{\cdot}01; \qquad \rho_{K_2O,U\cdot Na_2O} = +0{\cdot}93; \qquad \rho_{K_2O,Na_2O\cdot U} = +0{\cdot}82$$

The above calculations indicate that in volcanic rocks of Lassen Park, uranium correlates with potassium. Besides, the higher the values of potassium, the higher

Table 2. Calculations of the coefficient of correlation between Na_2O and U

	Na_2O	U	Na_2O^2	U^2	$Na_2O \times U$*	$Na_2O + U$	$(Na_2O + U)^2$
	3·26	1·0	10·63	1·00		4·26	18·15
	3·83	1·3	14·67	1·69		5·13	26·32
	4·13	1·4	17·06	1·96		5·53	30·58
	4·36	1·6	19·01	2·56		5·96	35·52
	3·88	1·7	15·05	2·89		5·58	31·14
	3·70	1·8	13·69	3·24		5·50	30·25
	3·81	1·9	14·52	3·61		5·71	32·60
	3·80	2·0	14·44	4·00		5·80	33·64
$n = 19$	4·29	2·1	18·40	4·41		6·39	40·83
	4·27	2·1	18·23	4·41		6·37	40·58
	4·29	2·2	18·40	4·84		6·49	42·12
	4·32	2·2	18·66	4·84		6·52	42·51
	4·53	2·5	20·52	6·25		7·03	49·42
	4·80	2·6	23·04	6·76		7·40	54·76
	4·54	3·0	20·61	9·00		7·54	56·85
	4·73	3·1	22·37	9·61		7·83	61·31
	4·43	3·2	19·62	10·24		7·63	58·22
	4·58	3·2	20·98	10·24		7·78	60·53
	4·30	3·6	18·49	12·96		7·90	62·41
	79·85	42·50	338·39	104·51	182·41	122·35	807·74

$$\overline{Na_2O} = \frac{79{\cdot}85}{19} = 4{\cdot}203 \qquad \nu_{Na_2O,U} = \frac{182{\cdot}41}{19} = 9{\cdot}600$$

$$\overline{U} = \frac{42{\cdot}50}{19} = 2{\cdot}237 \qquad \sigma_{Na_2O} = \sqrt{\nu^{(2)}_{Na_2O} - \overline{Na_2O}^2} = 0{\cdot}38$$

$$\nu^{(2)}_{Na_2O} = \frac{338{\cdot}39}{19} = 17{\cdot}810 \qquad \sigma_U = \sqrt{\nu^{(2)}_U - \overline{U}^2} = 0{\cdot}705$$

$$\nu^{(2)}_U = \frac{104{\cdot}51}{19} = 5{\cdot}501 \qquad \mu_{Na_2O,U} = \nu_{Na_2O,U} - \overline{Na_2O \cdot U} = +\,0{\cdot}198$$

$$r = +\frac{0{\cdot}198}{0{\cdot}38 \times 0{\cdot}705} \approx +\,0{\cdot}74$$

* Products additions on the counter of the arithmometer.

the values of uranium. A geochemical correlation between sodium and uranium is absent. The significant correlation between sodium and uranium calculated without taking into account the quantity of potassium is brought about by a strong correlation between the values of sodium and potassium.

Paragenetic relations of Na_2O, K_2O and U may be interpreted geochemically as follows. Fractional differentiation of magmas leads to a simultaneous concentration of Na_2O and K_2O in the course of magmatic evolution. At the same time the migration of U takes place through the magmatic basin. In the course

Table 3. Calculations of the equation $U' = a + C_1Na_2O + C_2K_2O$

	Na_2O	K_2O	U	$Na_2O + K_2O + U$	$(Na_2O + K_2O + U)^2$	U′	$(U-U')^2$	$\delta=\frac{U-U'}{S}$
	3·26	1·26	1·0	5·52	30·47	0·9	0·01	+0·5
	3·83	1·76	1·3	6·89	47·47	1·5	0·04	−1·1
	4·13	1·44	1·4	6·97	48·58	1·1	0·09	+1·6
	4·36	1·89	1·6	7·85	61·62	1·7	0·01	−0·5
	3·88	1·93	1·7	7·51	56·40	1·7	0·00	0·0
	3·70	1·95	1·8	7·45	55·50	1·7	0·01	+0·5
	3·81	2·05	1·9	7·76	60·22	1·9	0·00	0·0
	3·80	2·15	2·0	7·95	63·20	2·0	0·00	0·0
	4·29	2·39	2·1	8·78	77·09	2·3	0·04	−1·1
	4·27	2·52	2·1	8·89	79·03	2·4	0·09	−1·6
	4·29	2·16	2·2	8·65	74·82	2·0	0·04	+1·1
	4·32	2·53	2·2	9·05	81·90	2·4	0·04	−1·1
	4·53	2·80	2·5	9·83	96·63	2·8	0·09	−1·6
	4·80	2·65	2·6	10·05	101·00	2·6	0·00	0·0
	4·54	2·99	3·0	10·53	110·88	3·0	0·00	0·0
	4·73	2·91	3·1	10·74	115·35	2·9	0·04	+1·1
	4·43	3·11	3·2	10·74	115·35	3·1	0·01	+0·5
$n = 19$	4·58	2·95	3·2	10·73	115·13	3·0	0·04	+1·1
	4·30	3·34	3·6	11·24	126·34	3·4	0·04	+1·1
S	79·85	44·78	42·50	167·13	1516·98	42·4		
SS	338·39	111·60	104·51	1516·98				
S^2/n	335·58	105·54	95·07	1470·13				
SSD	2·81	6·06	9·44	46·85				
		Na_2O,K_2O	Na_2O, U					
SP		191·32	182·41	Check:				
S_iS_j/n		188·19	178·62	2·81 + 6·06 + 9·44				
SPD		3·13	3·79	+2 × 3·13				
			K_2O, U	+2 × 3·79				
SP			107·50	+2 × 7·33				
S_iS_j/n			100·17	46·81				
SPD			7·33					
S/n	4·20	2·36	2·24					

$$\Delta = \begin{vmatrix} 2·81 & 3·13 \\ 3·13 & 6·06 \end{vmatrix} = 7·23 \qquad \Delta b_1 \begin{vmatrix} 3·79 & 3·13 \\ 7·33 & 6·06 \end{vmatrix} = 0·028$$

$$\Delta b_2 = \begin{vmatrix} 2·81 & 3·79 \\ 3·13 & 7·33 \end{vmatrix} = 8·73$$

$$U' = 2·237 + 0·004(Na_2O \quad -4·203) + 1·208(K_2O \quad -2·357)$$

$$S = \sqrt{\frac{\Sigma(U - U')^2}{n - 3}} \approx 0·19$$

of this migration uranium is kept back by the medium enriched by potassium. The latter keeps back uranium as a linear function of the quantity of potassium.

The mechanism of uranium migration is not clear, but it is one that explains simultaneous concentration of uranium and potassium with the correlation between sodium and uranium lacking. The given mechanism is possibly a process of thermal diffusion, but this question must be investigated specially.

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The removal of soluble silica from fresh water entering the sea*

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Abstract—Determinations of soluble silica and chlorosity of water samples collected in and around the east Mississippi Delta showed that most of the soluble silica was removed from river-water by some process other than dilution with sea-water. While biological uptake by diatoms can account for part of this removal, it is more likely that a major portion is removed by inorganic precipitation.

Laboratory experiments with river-water and sea-water showed that both suspended matter from the river and electrolytes in sea-water are necessary for maximum inorganic precipitation. It is concluded that this process is an adsorption of soluble silica on suspended matter as it comes in contact with electrolytes, rather than a simple formation of salts with electrolytes. The inorganic removal can increase by a maximum of 4·5 per cent the weight of sediment in the water which may be expected to reach the bottom.

Introduction

The concentration of soluble silica in river-water is generally ten to fifteen times that of surface-water in the open ocean. The soluble silica concentration of Mississippi river-water averages 4–7·5 p.p.m., while the average concentration in Gulf of Mexico surface sea-water is 0·11 p.p.m. In spite of the large amount of soluble silica that is brought into the ocean, there is no sign of an accumulation of soluble silica in surface sea-water. Two hypotheses have been proposed to account for the depletion of soluble silica: biological removal and inorganic precipitation.

Biological removal of soluble silica from culture solutions by diatoms has been shown by Jorgensen (1953). Also, Armstrong (1954) and others have shown that following the spring "blooming" of diatoms in the English Channel the concentration of soluble silica in surface water was much reduced. Krauskopf (1956) concludes that because no dissolved silica was precipitated when he added silica solutions to sea-water, biological removal must be the main factor in preventing the accumulation of silica in sea-water. Moreover, during the initial mixing of river-water, before biological removal can occur, it might be expected that the concentration of soluble silica would decrease only because of dilution. If only dilution occurred, the concentration of soluble silica would be a linear function of dilution, as measured by chlorosity determination. Any deviation from linearity would be a measure of the extent of removal.

Such a linear relationship was found by Maeda and his associates (Maeda 1952, 1953; Makimoto *et al.*, 1955). However, their data only cover the chlorinity range from 5–17‰, which does not represent the complete range.

We have had an opportunity to test the dilution hypothesis at chlorinities of 0·1–21‰ in the area of the eastern Mississippi River Delta at Pass a Loutre, where the river empties into the Gulf of Mexico. We have also made measurements of

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phytoplankton production from which we have attempted to calculate the magnitude of silicate removal by phytoplankton and furthermore we have studied possible inorganic removal processes in the laboratory, using water samples from the Delta. Our results are reported in this paper.

Methods and Materials

Water samples were obtained in the field at stations shown in Fig. 1. One portion of each sample was drawn off into a glass citrate bottle, stoppered, and returned to the laboratory for the determination of chlorinity by tritation with silver nitrate. Chlorosity was calculated from this determination.

A second sub-sample was drawn from each Nansen bottle and filtered through a molecular filter (Millipore, type HA) having an average pore size of 0·45 μ. The filtrate was placed in a polyethylene bottle and returned to the laboratory for analysis of soluble silica. Experiments with sodium silicate solutions of known concentration indicated that no significant increase in soluble silica concentration occurred due to contact of water samples with the glass of the filter holders and evacuation flasks.

Soluble silica concentration was determined by the method of Dienert and Wandenbulcke (1923). Light absorption was measured with a Beckman Model-DU spectrophotometer at a wavelength of 360 mμ and extinction coefficients were corrected for "salt error". These "salt errors" are different for different salinities and are not a linear function of chlorosity. Beer's law slopes were, therefore, determined at different chlorosities and the "salt error" corrections applied at different chlorosities were determined from these plots. Duplicate determinations of soluble silica agreed within 5 per cent, but because of a high and variable blank correction, the values given are accurate to only ± 2 μmoles/l. Soluble silica was defined as the portion of the total silica which formed silicomolybdic acid in the presence of ammonium molybdate and sulphuric acid. According to Roy (1954) and Alexander, Heston and Iler (1954), only the silicate that is in true solution and in the ionic form will react with these reagents.

The possibility that, upon contact with sulphuric acid during colour development, more silica was dissolved from colloidal material which might pass the molecular filter was tested by comparing filtered river-water with dialysed river-water. Both the filtrate and the dialysate contained the same amount of soluble silica. Thus it is unlikely that such dissolution occurred.

Phytoplankton production was determined by the method of Steeman-Nielsen (1952) using ^{14}C. Phytoplankton production in the Delta will be the subject of another paper (Thomas and Simmons, in preparation). Only a range of values for production obtained immediately off Pass a Loutre is used in this paper for the calculation of biological uptake of soluble silica.

A sample of surface river-water for laboratory experiments on inorganic removal was collected at Station C-2 (see Fig. 1.). It had a chlorosity of 0·035 g Cl^-/l. and contained 82·06 μmoles soluble silica/l. A surface-water sample from the Gulf of Mexico was collected east of the Delta beyond the area shown in Fig. 1. The exact location is not known. This sample had a chlorosity of 20·61 g Cl^-/l. and contained only a trace of soluble silica. Both river and Gulf samples were stored in polyethylene carboys until used. Biological activity was stopped by the addition of 1 p.p.m. $HgCl_2$ to these samples. Since soluble silica concentrations did not change during several months storage, treatment with $HgCl_2$ was successful in stopping biological activities.

Results and Discussion

(a) *Field data*

Fig. 1 shows the station locations at which water samples were obtained during three different field trips. Tables 1, 2 and 3 summarize the results of the soluble silica and chlorosity determinations. Plots of soluble silica versus chlorosity for the various groups of data are shown in Figs. 2, 3 and 4.

The straight, dashed line on each graph indicates the line around which the points should group if the soluble silica of the river-water were merely diluted upon

Fig. 1. Chart showing station locations in the vicinity of Pass a Loutre sub-delta of the Mississippi River. Stations B-16, B-17, and B-18 are respectively 4, 8 and 12 statute miles due east of Station B-15.

mixing with open Gulf water. This line is obtained in each instance from average values of chlorosity and soluble silica in the open Gulf water and "typical" river-water.

Determinations of the chlorosity of open Gulf water over several field seasons have shown that it varies relatively little—averaging 20·4 g Cl^-/l., with a standard deviation of 0·5 g/l. The soluble silica concentration of open Gulf water averages 4·2 μmoles/l. and has a standard deviation of 3·1 μmoles/l.

Values of chlorosity and soluble silica of river-water are constant at any given time, but vary considerably throughout the year. In general, they are proportional to the amount of river discharge. As a result, the constants of the straight lines showing the theoretical relationship between soluble silica and chlorosity are determined entirely by the characteristics of the river-water.*

* Our values of soluble silica in Mississippi river-water varied from 65 to 120 μmoles of silica/l. (4–7·5 p.p.m.), which is in excellent agreement with the values of SCHWARTZ (1938) and slightly lower than the earlier values of CLARKE (1924).

Table 1. Silicate and chlorosity data of June 1953

Station	Depth (ft)	Soluble silica μmoles/l.	Chlorosity (g Cl^-/l.)	Station	Depth (ft)	Soluble silica μmoles/l.	Chlorosity (g Cl^-/l.)
A-1	0	78·6	0·2	A-12	0	73·2	0·2
A-1	7·5	80·7	0·2	A-12	5	11·0	14·4
A-2	0	82·0	0·2	A-12	10	7·7	16·0
A-2	12	70·2	0·2	A-12	25	7·3	18·8
A-3	0	77·5	0·2	A-12	36	11·0	13·9
A-3	16	76·0	0·2	A-13	0	72·8	0·4
A-4	0	76·3	0·2	A-13	5	31·3	8·4
A-4	7·5	76·8	0·2	A-13	10	6·2	14·8
A-5	0	76·0	0·4	A-13	25	4·2	18·2
A-5	3	64·3	2·0	A-13	40	3·8	20·2
A-5	6	35·2	9·0	A-14	0	36·0	8·4
A-6	0	72·8	0·3	A-14	5	10·3	15·0
A-6	5	32·2	9·0	A-14	10	6·5	16·0
A-6	10	11·8	14·7	A-14	25	9·7	18·9
A-6	25	6·3	18·0	A-14	40	9·8	19·0
A-6	40	9·5	18·7	A-15	0	72·3	1·0
A-7	0	68·3	0·7	A-15	5	19·7	12·4
A-7	5	28·8	8·9	A-15	10	7·3	15·6
A-7	10	12·0	14·1	A-15	25	4·0	18·3
A-7	25	2·8	18·0	A-15	40	7·0	18·5
A-7	40	2·8	18·9	A-15	85	8·3	20·3
A-7	104	8·2	20·2	A-16	0	71·2	0·7
A-8	0	51·0	4·9	A-16	5	4·5	16·7
A-8	5	18·5	13·1	A-16	10	2·7	18·1
A-8	8	17·7	14·5	A-16	25	4·0	19·4
A-9	0	66·7	1·4	A-16	40	2·8	20·2
A-9	5	29·3	10·0	A-16	100	8·8	20·4
A-9	7	16·2	13·7	A-16	188	7·0	20·5
A-10	0	72·8	0·3	A-16	0	56·7	2·9
A-10	5	47·8	5·8	A-17	0	6·5	15·8
A-10	7	22·3	13·0	A-17	5	2·8	18·8
A-11	0	73·5	0·8	A-17	10	1·5	19·7
A-11	5	9·7	15·6	A-17	25	2·0	19·9
A-11	10	7·5	16·6	A-17	40	2·3	20·1
A-11	25	7·3	17·7	A-17	100	3·0	20·5
A-11	40	8·5	18·7	A-17	188	5·0	20·3

A consideration of Figs. 2, 3 and 4 leads to the conclusion that the observed distribution of soluble silica as a function of chlorosity (dilution) differs significantly from that which would be expected from the hypothesis that the soluble silica of the river-water is merely diluted upon mixing with Gulf water. Even if the slope of the theoretical dilution line shown in these figures is changed to take the error (± 2 μmoles) of the determination of soluble silica into account, significant deviations from this straight line still exist and the results cannot be explained on the basis of experimental error.

Table 2. Silicate and chlorosity data of July 1955

Station	Depth (ft)	Soluble silica (μmoles/l.)	Chlorosity (g Cl^-/l.)
B-1	0	114	0·62
B-1	5	113	0·63
B-1	10	114	0·62
B-1	15	118	0·63
B-1	20	113	0·63
B-1	25	115	0·63
B-2	0	110	0·58
B-3	0	108	0·66
B-4	0	110	0·61
B-5	0	110	0·66
B-6	0	109	1·02
B-7	0	110	1·20
B-8	0	105	2·20
B-9	0	101	2·24
B-10	0	99·9	2·66
B-11	0	79·7	5·08
B-11	5	20·9	13·2
B-11	10	22·9	13·9
B-11	15	6·0	16·6
B-11	20	3·0	17·8
B-11	25	6·5	18·2
B-12	0	96·7	3·33
B-13	0	89·6	3·87
B-14	0	75·1	5·92
B-15	0	85·0	4·66
B-15	5	24·1	13·6
B-15	10	4·8	16·9
B-15	15	7·6	16·8
B-15	20	5·2	16·4
B-15	25	3·0	18·0
B-16	0	61·9	7·68
B-16	5	12·3	15·4
B-16	10	7·0	16·0
B-16	15	2·8	17·2
B-16	20	1·2	18·0
B-16	25	1·4	18·3
B-17	0	27·4	11·6
B-17	5	4·8	16·6
B-17	10	5·0	16·5
B-17	20	0·6	17·8
B-17	25	0·8	18·2
B-17	37	0·4	18·4
B-18	0	7·4	17·0
B-18	5	1·8	17·0
B-18	10	1·8	17·1
B-18	20	0·6	17·8
B-18	40	0·6	18·5
B-18	70	2·0	20·4

Table 3. Silicate and chlorosity data of October 1955

Station	Depth (ft)	Soluble silica (μmoles/l.)	Chlorosity (g Cl^-/l.)
C-1	0	63·9	1·6
C-2	0	59·3	2·4
C-3	0	56·1	6·1
C-4	0	41·9	7·1
C-5	0	7·5	14·8
C-6	0	8·2	16·8
C-7	0	4·6	177·5

The concentration of soluble silica as a function of chlorosity in these waters (the data of Figs. 2, 3 and 4 and Tables 1, 2 and 3) can be described (with experimental error) by the equations:

$$(SiO_2)_f = (SiO_2)_R - B\,(Cl) + C\,(Cl)^2; \qquad B > C \tag{1}$$

where $(SiO_2)_f$ is the soluble silica concentration found, (Cl) is the chlorosity, $(SiO_2)_R$ is the initial concentration in the river and B and C are constants that vary seasonally (Bien, 1953). These data can also be expressed (within experimental error) by three lines OA, and BC in Fig. 5. Line OA represents the initial removal, AB, further removal, BC, the final dilution of the water and OC, the theoretical dilution curve. A consideration of this plot shows that nearly all of the soluble silica is removed. If only a portion were removed during the initial mixing (line OA)

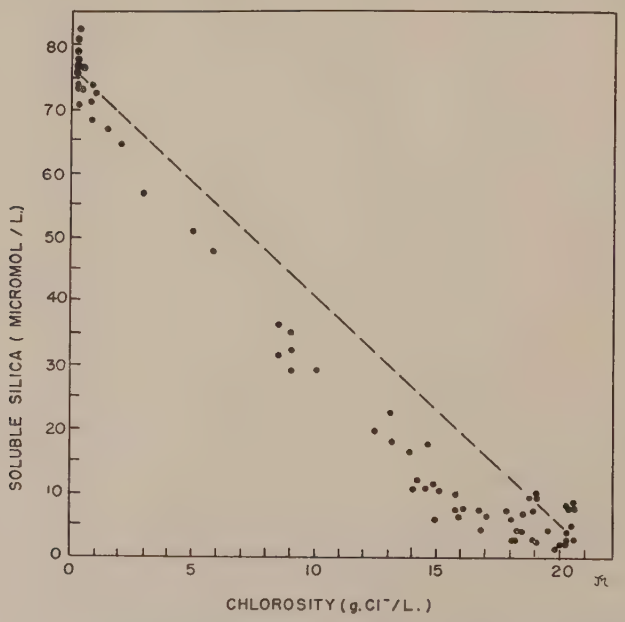

Fig. 2. Soluble silica concentration as a function of chlorosity of water samples. Data of June 1953.

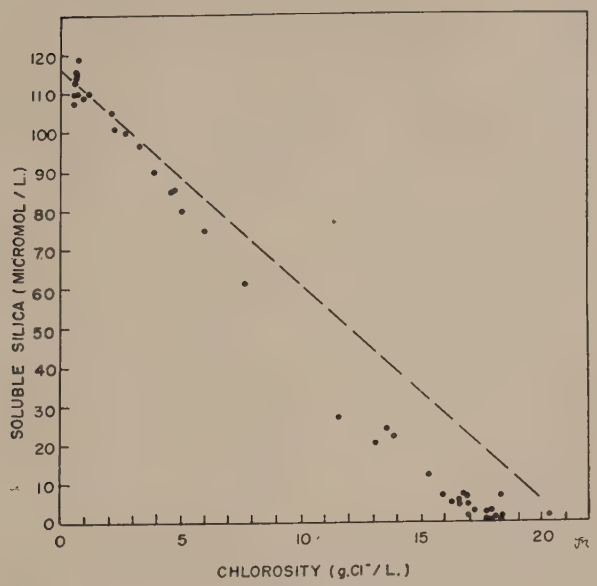

Fig. 3. Soluble silica concentration as a function of chlorosity of water samples. Data of July 1955.

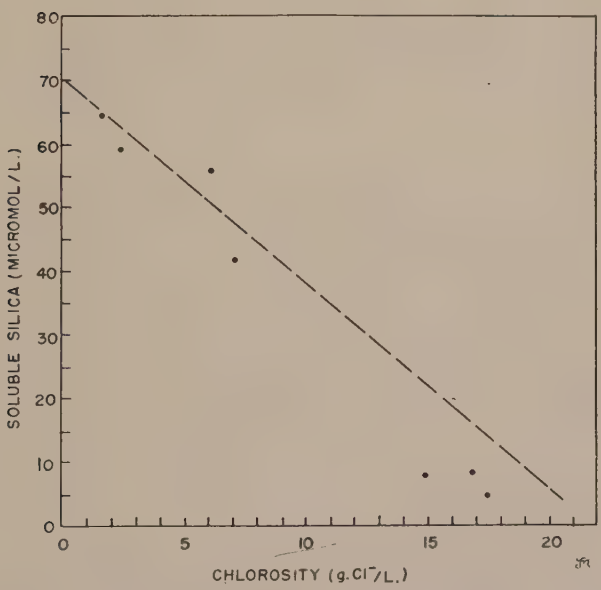

Fig. 4. Soluble silica concentration as a function of chlorosity of water samples. Data of October 1955.

and thereafter only dilution occurred, the experimental points should follow line AC. Instead, they do not fall on such a line, but a minimum value for soluble silica is reached before maximum dilution has occurred (at point B). Any further dilution with sea-water (line BC) results in no more removal, since the sea-water already contains this minimum amount. Since removal ceases, the removal process

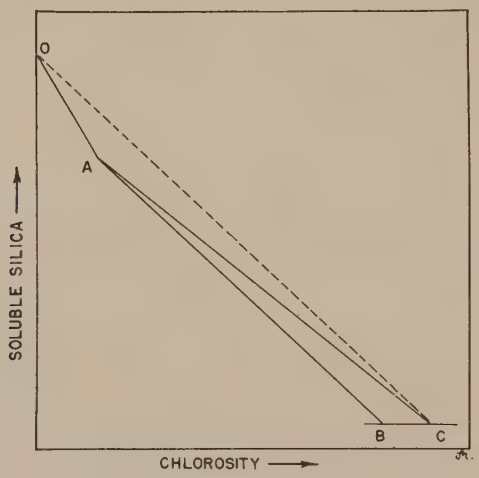

Fig. 5. Illustrative relationships of soluble silica to chlorosity.

must be complete, and all of the soluble silica originally present must have been precipitated. This does not mean that dilution does not occur, but, that as fast as river-water is diluted, its soluble silica is removed. The possible causes of the initial removal (line OA) and of further removal (line AB) are discussed in section (c).

(b) *Laboratory experiments on inorganic removal processes*

Several experiments were performed which show that results similar to the field data can be obtained by mixing turbid river-water with sea-water. The experiments were carried out by withdrawing an aliquot from a sample of river-water and adding an equivalent volume of sea-water. The process was repeated at hourly intervals and each aliquot was then filtered and its concentration of soluble silica determined. Results obtained using Mississippi river-water and Gulf sea-water are shown in Table 4 and Fig. 6. These results are not due to biological uptake, since such activity was prevented by the addition of 1 p.p.m. $HgCl_2$. It should be noted that inorganic removal occurs within 1 hr, which indicates that it will occur quite rapidly in the field.

The same experiment was performed by mixing Mississippi river-water with Pacific Ocean surface sea-water collected 60 miles east of Guadalupe Island. This sample had a chlorosity of 18·04 g Cl^-/l., and contained 20·1 μmoles soluble silica/l. The results are shown in Table 5 and Fig. 7, and are similar to those obtained with Gulf of Mexico water. Thus the phenomenon of inorganic removal is very likely a general one and is not due to anything especially characteristic of Gulf water.

Two possible mechanisms by which inorganic removal of soluble silica might

Table 4. Soluble silicate and chlorosity data of dilution Experiment A

Experiment Nos. I		II		III		IV	
Chlorosity (g Cl^-/l.)	Soluble SiO_2 (μmoles/l.)	Chlorosity (g Cl^-/l.)	Soluble SiO_2 (μmoles/l.)	Chlorosity (g Cl^-/l.)	Soluble SiO_2 (μmoles/l.)	Chlorosity (g Cl^-/l.)	Soluble SiO_2 (μmoles/l.)
0·035	82·06	0·035	82·06	0·035	82·06	0·035	82·06
2·06	65·4	0·82	76·8	2·06	69·8	2·06	70·1
4·12	61·7	1·62	70·4	3·92	68·1	3·92	61·8
6·18	52·5	2·38	67·7	5·59	52·6	5·59	64·9
8·24	41·7	3·10	63·9	7·09	46·7	7·09	46·8
10·30	36·2	3·80	61·3	8·44	44·6	8·44	42·4
11·33	31·2	4·48	58·1	9·64	37·0	9·64	37·1
12·36	27·3	5·12	70·1	10·73	34·9	10·73	34·9
13·33	25·7	5·74	52·5	11·72	29·0	11·72	26·9
14·40	20·1	6·34	51·6	12·61	24·6	12·61	24·2
15·45	16·3	6·91	48·4	13·43	20·8	13·43	20·8
16·52	11·8	7·46	45·3	14·15	18·2	14·15	18·4
17·56	9·4	8·49	43·7	14·79	17·2	14·79	18·4
18·57	5·9	9·70	40·8	15·38	15·7	15·38	15·0
19·57	1·7	10·79	33·0	15·90	13·2	15·90	13·5
20·61	0	11·76	28·1	16·37	11·4	16·37	11·5
		12·65	28·1	16·79	9·4	16·79	9·1
		13·44	22·1	17·17	8·3	17·17	8·4
		14·16	20·5	17·52	6·6	17·52	6·5
				17·83	6·0	17·83	5·1
				18·11	4·4	18·11	3·1

occur are: (1) a reaction with electrolytes in sea-water resulting in polymerization or salt formation and (2) adsorption or co-precipitation with suspended solids or colloidal material in river-water as these come in contact with electrolytes in sea-water. We have used Millipore-filtered natural waters and artificial solutions in order to distinguish between these two processes.

When filtered sea-water was diluted to various chlorosities with distilled water and known amounts of sodium metasilicate (105 μmoles/l.) were added, no loss of soluble silica was observed after storage of the solutions for 1 week. Similar results were observed using sodium chloride solutions rather than filtered sea-water. These data are shown in Table 6. Successive dilution of a sodium metasilicate solution with a sodium chloride solution also did not result in inorganic removal (see Curve I, Fig. 8). Thus, electrolytes alone do not apparently cause inorganic removal.

In a further test of this hypothesis, filtered river-water was successively diluted with filtered Gulf water. These results are shown in Curve II, Fig. 8. The deviation from linearity observed was somewhat less than that observed using unfiltered waters and may be due to incomplete removal of colloidal material by the Millipore filter. Such material has been shown to be important in inorganic removal by

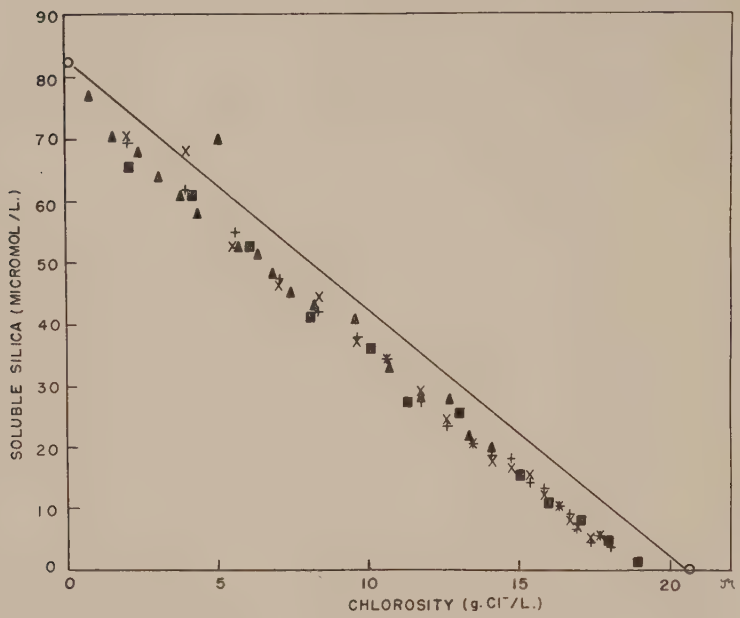

Fig. 6. Soluble silica concentration as a function of chlorosity as unfiltered river-water is mixed with Gulf of Mexico water in the laboratory.

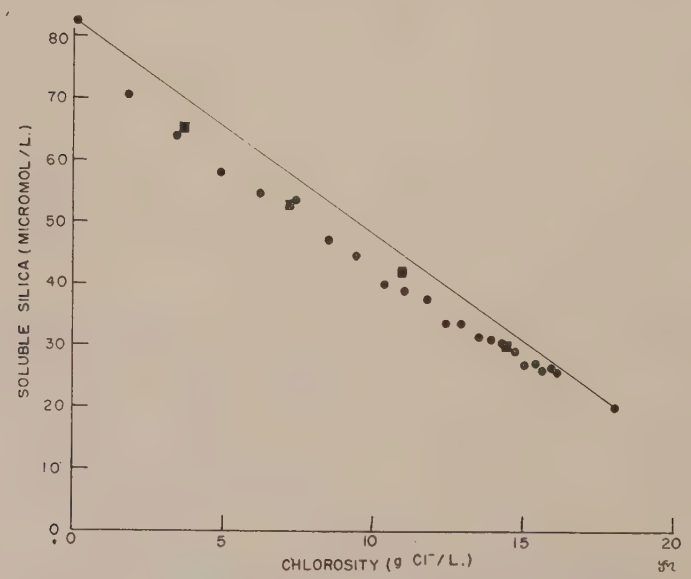

Fig. 7. Soluble silica concentration as a function of chlorosity as unfiltered river-water is mixed with Pacific Ocean water in the laboratory.

Table 5. Soluble silicate and chlorosity data of dilution Experiment B

Experiment Nos. I		II	
Chlorosity (g Cl^-/l.)	Soluble SiO_2 (μmoles/l.)	Chlorosity (g Cl^-/l.)	Soluble SiO_2 (μmoles/l.)
0·035	82·06	0·035	82·06
3·61	64·7	1·80	70·4
7·22	52·6	3·43	63·9
10·82	41·7	4·89	57·9
14·43	30·1	6·21	54·7
18·04	20·1	7·39	53·5
		8·41	46·9
		9·41	44·4
		10·28	39·9
		11·05	38·9
		11·75	37·5
		12·38	33·4
		12·95	33·4
		13·46	31·5
		13·92	31·1
		14·33	30·5
		14·70	29·5
		15·04	27·2
		15·34	27·3
		15·61	26·4
		15·85	26·8
		16·07	26·2

The sea-water used in this experiment had been standing in a glass bottle for over a year.

Table 6. Amounts of soluble silica found after storage for 1 week in the presence of filtered Gulf water or sodium chloride solutions. Amount added = 105 μmoles/l.

A. Filtered Gulf water plus distilled water

Chlorosity (g Cl^-/l.)	0	1·81	3·61	5·41	7·22	9·03	10·84	12·64	14·45	16·75	18·06
SiO_2 soluble found (μmoles/l.)	105·4	103·0	105·0	105·0	105·2	104·0	105·5	103·6	105·0	104·5	106·0

B. Sodium chloride solutions

Chlorosity (g Cl^-/l.)	0	2·12	4·24	6·37	8·49	10·61	12·73	14·85	16·98	19·10	20·22
SiO_2 soluble found (μmoles/l.)	105·0	103·5	106·2	104·5	104·8	105·4	106·1	102·6	106·0	105·2	105·0

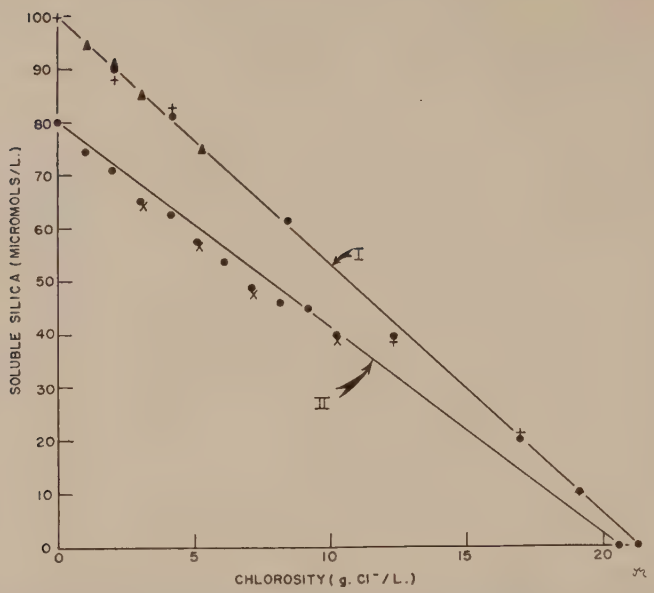

Fig. 8. Soluble silica dilution experiments. Curve I: Sodium silicate solution diluted with sodium chloride solutions. Curve II: Filtered river-water diluted with filtered sea-water. (Solid lines are calculated dilution curves.)

White *et al.* (1956). It may also mean that soluble silica is precipitated by the presence of a small amount of aluminium ions which passed the filter, formed aluminium hydroxide and co-precipitated the silica (Goto, 1956; Arrhenius, 1954; Okamoto *et al.*, 1957).

In general, these results agree with those of Krauskopf (1956), which showed that precipitation of dissolved silica does not occur when silica solutions are mixed with sea-water.

If adsorption of soluble silica could occur as suspended matter in the river reacted with electrolytes, inorganic removal would be observed when suspended solids were added to filtered sea-water enriched with sodium silicate. Such removal was observed upon addition of bentonite, aluminium oxide, and particularly, suspended solids from the Mississippi River, to enriched Gulf water. In these experiments, Gulf water was enriched, a concentrate of suspended material was added, the sample was shaken, and allowed to stand overnight. After standing, the suspension was filtered and soluble silica was determined. The results are shown in Table 7 and Fig. 9, and the data are corrected for the amount of soluble silica introduced with the concentrated suspended matter. It should be noted that suspended material from the river is more effective than either bentonite or aluminium oxide. Also, since the amount of removal increases with increasing amount of suspended solids from the river, inorganic precipitation is very likely an adsorption process.

The necessity of electrolytes as well as suspended matter for precipitation was demonstrated by adding solid sodium chloride to river-water to increase chlorosity. These results are shown in Table 8 and Fig. 10. As the chlorosity increased, an

Table 7. Removal of soluble silica by adding suspended solid matter to enriched sea-water (chlorosity = 16·27 g Cl^-/l.)

A. Bentonite suspension (suspension contains 0·102 g solid/ml; filtered solution contains 47·4 μmoles soluble silica/l.)

Wt. clay added (g/l.)	SiO_2 added (μmoles/l.)	SiO_2 found (μmoles/l.)	Per cent recovered
0	107·4	107·4	100·0
0·0204	107·6	101·6	94·3
0·0408	107·8	97·6	90·5
0·0612	108·0	96·5	89·2
0·0816	108·2	97·6	90·1
0·1024	108·4	95·2; 98·5	88·0; 90·5
0·1224	108·5	97·1	89·5
0·1530	108·7	95·6	88·0
0·204	109·3	102·5; 101·5; 97·5	93·0; 93·2; 90·5
0·306	110·4	101·2; 100·7	91·0; 90·0
0·408	111·2	102·0; 99·5	91·5; 89·5
0·510	112·1	104·3; 103·5; 101·2	98·0; 92·5; 90·0
0·612	113·0	105·0	93·0
0·714	114·0	105·3	92·5
0·816	115·0	104·8	91·0
0·918	115·9	104·8	90·5
1·02	117·0	104·8	89·5

B. Aluminium oxide suspension (suspension contains 0·120 g solid/ml; soluble silica added = 107 μmoles/l.)

Wt. Al_2O_3 added (g/l)	SiO_2 found (μmoles/l.)	Per cent recovered
0	107·0	100·0
0·024	104·0	97·4
0·048	100·0	94·0
0·072	95·5	89·0
0·096	101·0	94·5
0·12	99·5	93·5
0·144	100·3	94·1
0·168	100·3	94·1
0·192	99·7	93·5
0·216	100·0	94·0
0·240	99·7	93·5

Table 7 (*continued*)

C. River mud suspension (suspension contains 0·183 g solid/ml; filtered solution contains 95 μmoles soluble silica/l.)

Wt. Solid added (g/l.)	SiO_2 added (μmoles/l.)	SiO_2 found (μmoles/l.)	Per cent recovered
0	101·6	101·6	100·0
0·0732	101·97	98·3	96·5
0·1464	102·34	97·5	95·3
0·2196	102·72	97·5	95·0
0·2928	103·1	97·2	94·5
0·366	103·5	96·1; 95·2	93·0; 92·3
0·4392	103·8	95·2	92·8
0·5124	104·2	96·1	92·5
0·5856	104·6	96·1	92·0
0·6588	105·0	95·5	91·0
0·732	105·3	95·0; 92·5	90·2; 89·0
1·098	106·3	92·0	87·0

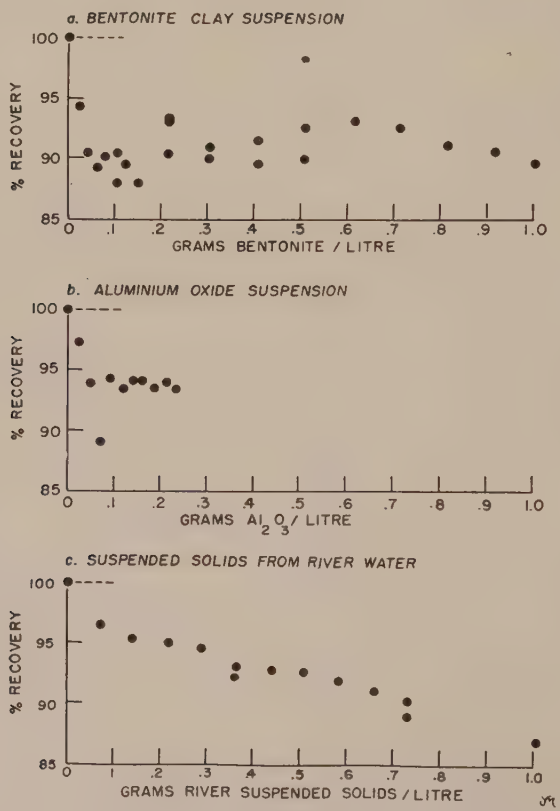

Fig. 9. The influence of suspended matter on the recovery of soluble silica from enriched Gulf of Mexico water.

Table 8. Soluble silica removal from river-water by sodium chloride

Chlorosity (g Cl^-/l.)	SiO_2 found (μmoles/l.)	Percent recovered
0·035	90·0	100·0
0·65	84·9	94·5
1·25	83·2; 85·6	92·5; 94·5
1·86	83·0; 82·8	92·3; 92·2
2·47	83·1; 82·8	92·4; 92·2
3·07	83·2; 83·0	92·5; 92·3
3·68	82·8; 80·5	92·0; 89·5
4·29	83·0	92·3

* Original soluble silica content of this water was 82·06 μmoles/l. This was increased to 90 μmoles/l. for the experiment.

initial drop in concentration was observed, after which the concentration remained constant.

The conditions of these experiments are different from those of KRAUSKOPF (1956), who also added suspended matter to silica solutions. Little or no removal occurred in his experiments when kaolinite, montmorillonite, calcite or Fe_2O_3 were added to silica solutions made up in distilled water. Our experiments show that both electrolytes (sea-water) and suspended matter are necessary. On the other hand, in KRAUSKOPF's experiments with silica-enriched artificial sea-water, Fe_2O_3 removed about the same amount of soluble silica as in our experiments (6–9 per cent), but calcite was without effect. It should be noted that the concentrations of soluble silica used in KRAUSKOPF's experiments are 25–35 times greater than those used in our experiments or found in river-water. Also, KRAUSKOPF does not state how much suspended matter was added to his solutions. It is probable that the concentrations of silica and suspended matter are critical in such experiments. In our experiments both the concentration of silica and suspended matter from the river approximate those found in the river. A problem which remains for investigation is the role of iron and aluminium in systems which approximate the natural river–ocean complex.

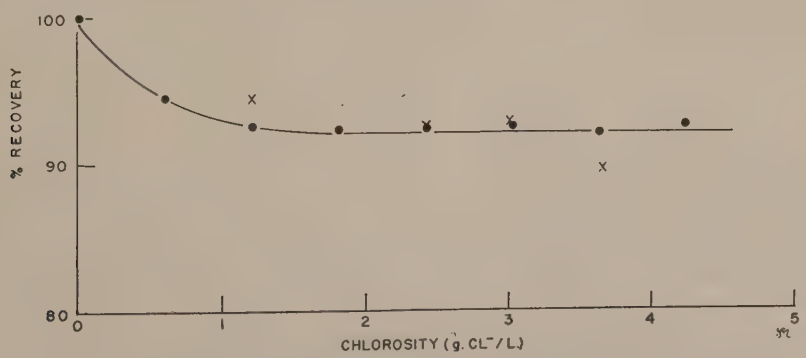

FIG. 10. The effect of sodium chloride on the soluble silica concentration of Mississippi river-water.

(c) *Biological removal of soluble silica by phytoplankton*

It is very difficult to estimate whether significant removal of soluble silica due to biological uptake by diatoms occurs during the *initial* mixing of river-water. About 15 per cent of the soluble silica in river-water or about 10–18 μmoles/l. are removed by processes other than dilution during mixing to a chlorosity of 8 g Cl^-/l. Our measurements (Thomas and Simmons, 1957) show that from 1 to 7 μmoles organic carbon are formed per litre per day by surface phytoplankton off Pass a Loutre. Most of the phytoplankton off Pass a Loutre are diatoms (Simmons and Thomas, 1957). Using a factor for the ratio between carbon and silica atoms in diatoms (100 : 40) calculated from Sverdrup *et al.* (1942, p. 234), we can calculate that between 0·40 and 2·80 μmoles of silica are taken up per litre per day by diatoms. Thus about 2 per cent of the total soluble silica in river-water might be taken up in 1 day by offshore diatoms or about 20 per cent of the initial removal process might be due to diatom uptake if the assumption is made that it takes 1 day for 1 l. of fresh river-water to be diluted to a chlorosity of 8 g Cl^-/l.

This assumption is almost certain to be true during periods of high river discharge. According to Scruton (1956), the average surface current at the mouth of North Pass during June 1953 was 2 knots. This velocity would decrease to less than 1 knot as the water moved seaward. Thus 1 l. of water might move seaward some 24 miles during 1 day. The existence of a thin layer of relatively fresh turbid water (chlorosity 1·3 g Cl^-/l.) during the season of high river discharge even tens of miles off the delta (Scruton and Moore, 1953; Thomas and Simmons, 1957) indicates that mixing to a chlorosity of 8 g Cl^-/l. does not occur during the movement of the water for 24 miles.

At a period of low discharge, the above assumption is probably not true. The current velocity is less than half that measured during high river discharge (Scruton, 1956), so that 1 l. of river-water might move only 12 miles during 1 day. However, our measurements show that a layer of relatively fresh water does not extend that far offshore (Thomas and Simmons, 1957) during the fall months.

Mixing to the *final* chlorosity probably takes several days at all seasons. Thus biological uptake may account for an appreciable amount of silica in the complete process. When the field results and the laboratory results are expressed on a comparable basis, there is a difference between the two sets of data, which may be attributed to biological uptake, since biological activities were stopped by the addition of mercuric chloride in the laboratory experiments. In comparing the sets of data, we have used the following equations:

$$(SiO_2)_{Cl} = (SiO_2)_R - K(Cl) \qquad (2)$$

is the equation describing the theoretical dilution of soluble silica in river-water with Gulf water. In this equation $(SiO_2)_{Cl}$ is the theoretical concentration which should be found at a given chlorosity (Cl); $(SiO_2)_R$ is the initial concentration in the river-water, and K is a constant. Another equation represents the soluble silica actually found, at a given chlorosity, $(SiO_2)_f$, and was given by equation (1) in section (a). The final equation used is that expressing the theoretical dilution if river-water is diluted with Gulf water containing no silica:

$$(SiO_2)'_{Cl} = (SiO_2)_R - K'(Cl) \qquad (3)$$

in which K' is slightly greater than K. This is used because we are only interested in the removal of silica from river-water and thus can neglect possible removal from Gulf water. The per cent removal is then calculated from the difference between $(SiO_2)_{Cl}$ and $(SiO_2)_f$ by dividing this value by $(SiO_2)_{Cl}$ and multiplying by 100.

Table 9 shows these calculations for the field data; Table 10, those for the experiments in which river-water was successively diluted with Gulf water. The field and experimental results are compared in Fig. 11. The difference between the

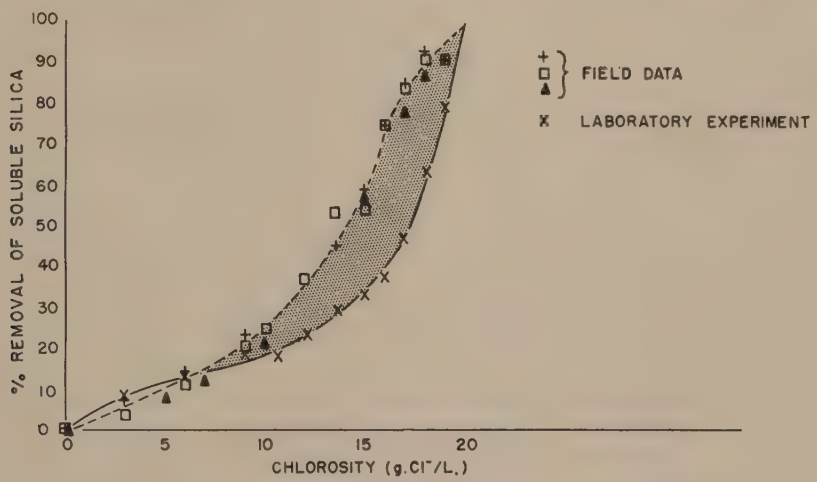

Fig. 11. The percentage removal of soluble silica as a function of chlorosity.

two sets of data is shown by cross-hatching. It should be noted that below a chlorosity of 8 gm Cl^-/l. little or no difference is found, but beyond this point the difference is considerable. This supports previous estimates that biological activity will occur only in waters of high chlorosity in which sufficient time for uptake has elapsed. An alternative explanation for the difference between the two curves is that in the laboratory experiments there may not be enough time for maximum removal to occur, since the river-water and Gulf water were only mixed for 1 hour before soluble silica was determined. However, if this is the reason for the difference, the initial percentage removal for one set of data should not agree so well with that for the other set.

Conclusions

When fresh water enters the sea, it would be expected that the high concentration of soluble silica in fresh water could be reduced by dilution with sea-water having a low concentration of soluble silica. However, the soluble silica concentration is reduced by some process other than dilution. Two such processes can occur: biological uptake or inorganic precipitation.

Calculations based on phytoplankton production measurements and estimates of mixing rates of water masses in the Mississippi Delta area show that biological removal may possibly account for some of the *initial* removal during periods of high river discharge. During periods of low river discharge such removal is less possible.

However, after the initial mixing, at chlorosities greater than 8 g Cl^-/l., biological removal may be appreciable, since enough time could elapse for uptake by diatoms to occur. Much more extensive work would be required to distinguish definitely between biological uptake and inorganic precipitation in the field.

Two mechanisms of inorganic precipitation of soluble silica have been proposed: (1) reaction of soluble silica with electrolytes in sea-water resulting in salt formation or (2) adsorption or co-precipitation of soluble silica with suspended solids or

Table 9. The difference between calculated and observed values for soluble silica as a function of chlorosity. Data from field samples

Chlorosity (g Cl^-/l.)	$(SiO_2)_{Cl}$ (μmoles/l.)	$(SiO_2)_f$ (μmoles/l.)	$\Delta(SiO_2)$ $(SiO_2)_{Cl}-(SiO_2)_f$ (μmoles/l.)	$(SiO_2)'_{Cl}$ (μmoles/l.)	% Removal $100\,(\Delta\,SiO_2)/(Si)'_{Cl}$
A—Dates of June 1953					
0·2	76·4	76·4	0	76·4	0
3·0	66·4	61·8	4·6	68·8	7·0
6·0	55·7	48·0	7·7	54·5	14·0
9·0	44·9	35·0	9·8	43·1	23·0
10·0	41·4	31·2	10·2	39·3	25·7
12·0	34·2	22·5	11·7	31·8	36·8
13·5	28·8	17·0	11·8	26·0	45·0
15·0	23·5	11·5	12·0	20·9	59·0
16·0	19·9	7·5	12·4	16·6	74·7
17·0	16·4	5·6	10·8	12·8	84·3
18·0	12·8	4·4	8·9	9·1	92·3
19·0	9·2	4·4	4·8	5·3	90·6
B—Data of July 1955					
0·6	113	113	0	0	0
3·0	99·6	96·0	3·6	101·3	3·5
6·0	82·8	74·0	8·8	82·2	10·7
9·0	66·0	53·0	13·0	65·0	20·0
10·0	60·4	46·0	14·4	59·3	24·3
12·0	49·1	31·0	18·1	47·9	37·9
13·5	40·8	20·0	20·8	39·3	53·0
15·0	32·3	12·0	20·3	30·8	53·5
16·0	26·8	8·0	18·8	25·1	75·0
17·0	21·2	5·0	16·2	19·4	83·5
18·0	15·5	3·0	12·5	13·7	91·3
19·0	9·4	2·0	7·4	8·1	91·5
C—Data of October 1955					
0	70	70	0	70	0
5	54	50	4	53	7·5
7·0	47·4	42	5·4	46	12·0
10·0	37·7	30	7·7	36	21·0
15·0	21·6	11	10·6	18·5	57·0
17·0	15·0	5·6	9·4	12·0	78·0
18·0	12·0	5·0	7·0	8·0	87·0

The difference between calculated and observed values for soluble silica as a function of chlorosity. Data from laboratory experiments

Chlorosity (g Cl^-/l.)	$(SiO_2)_{Cl} = (SiO_2)'_{Cl}$ (μmoles/l.)	$(SiO_2)_f$ (μmoles/l.)	$\Delta(SiO_2)$ (μmoles/l.)	% Removal $\frac{1000s}{SR}$
0	82·1	82·1	0	0
3	70·1	64·4	5·7	8·1
6	58·2	51·2	7·0	12·0
9	46·2	39·3	8·9	19·3
10·5	40·2	33·1	7·1	17·7
12·0	34·3	26·2	8·1	23·6
13·5	28·3	20·0	8·3	29·3
15·0	22·3	15·0	7·3	32·8
16·0	18·3	11·3	7·0	37·8
17·0	14·3	7.5	6·8	47·5
18·0	10·4	3·75	6·6	63·4
19·0	6·3	1·25	5·0	79·5

colloidal material in river-water as these come in contact with electrolytes. Our data show that both electrolytes and colloidal or suspended solids are necessary for maximum inorganic removal. The fact that increasing removal occurs when the amounts of suspended solids are increased indicates that adsorption or co-precipitation of soluble silica on these solids probably occurs.

These precipitation processes result in the removal of almost all of the soluble silica from river-water. Since this river-water contains from 4 to 7·5 mg/l. soluble silica and 160 to 1500 mg/l. of suspended solids are present in the river-water, the weight of suspended material in these waters can be slightly increased by these processes, and therefore presumably some of the silica in the deltaic sediments would also be derived from these processes.

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Biogeochemistry of the rare-earth elements with particular reference to hickory trees*

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Abstract—Hickory trees concentrate the rare-earth elements in their leaves to a phenomenal degree and may contain as much as 2300 p.p.m. of total rare earths based on the dry weight of the leaves. The average proportions of the individual elements (atomic percent of the total rare-earth elements) in the leaves are: Y 36, La 16, Ce 14, Pr 2, Nd 20, Sm 1, Eu 0·7, Gd 3, Tb 0·6, Dy 3, Ho 0·7, Er 2, Tm 0·2, Yb 1, and Lu 0·2. The similarity in the proportions of the rare-earth elements in the leaves and in the exchange complex of the soil on which the hickory trees grow indicates that the trees do not fractionate the rare earths appreciably.

The variation of the rare-earth elements in the leaves and soils can be explained generally in terms of the relative abundance of the cerium group and the yttrium group, except for the element cerium. The large fluctuations in the proportion of cerium [Ce/(La + Nd) atomic ratios of 0·16 to 0·86] correlate with oxidation-reduction conditions in the soil profile. The substitution of dilute H_2SO_3 for dilute HCl in the determination of available rare-earth elements brings about a large increase in the proportion of cerium that is extracted from an oxygenated subsoil. These relationships strongly suggest that quadrivalent cerium is present in oxygenated subsoil and is less available to plants than the other rare-earth elements that do not undergo such a change in valence.

A few parts per billion of rare-earth elements have been detected in two samples of ground water.

Introduction

The widespread occurrence of the rare-earth group of elements at a concentration level of a few hundred p.p.m. in the common rocks and in soils is now well appreciated, and a rough outline of the geochemistry of these elements in the lithosphere has become established (Goldschmidt, 1954, Rankama and Sahama, 1950). The occurrence of rare-earth elements in plants has occupied the attention of only a few investigators. Robinson *et al.* (1938) reported on the extraordinary concentration of rare earths in the leaves of some hickory trees, amounting to as much as 2300 p.p.m. of the dry weight of the leaves. Most plants contain less than 60 p.p.m. of total rare earths in their leaves.

We have now used emission spectrochemical methods for quantitative determination of the individual rare-earth elements that are concentrated in hickory leaves and those present as exchangeable cations in the soils on which the hickory trees grow. The purpose of the work was to determine if hickory trees have any marked preference for certain of the rare-earth elements among those available to them in the soil. To a first approximation, our preliminary results indicate no marked selectivity on the part of the hickory trees. Further work may show a minor degree of biological fractionation not now discernible in the limited data available. The study has also revealed unexpected major fluctuations in the proportion of cerium, which seem to be related to changes in the valence of this element under soil conditions.

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Previous Work

Cossa (1878) first reported small quantities of rare earths in barley, beechwood, rice and in the leaves of tobacco and grape. Goldschmidt and Peters (1933) found rare earths enriched in coal ashes and assumed that these had been concentrated by plants. Robinson (1914) reported 100–800 p.p.m. total rare earths in many soils of the United States, and Robinson, Whetstone and Scribner (1938) reported 2000 p.p.m. (dry weight basis) rare earths in hickory leaves. Scribner (1939) identified Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Er and Yb in the total rare earths chemically separated from the leaves. Of these Y, La, Ce and Nd were the major constituents. Borneman–Starinkevitch *et al.* (1941) found a nearly constant amount of 200 p.p.m. rare earths in all Russian soils examined. They reported that the ash of whole plants showed from 2 to 30 p.p.m. and the ash of green parts of the plants, from 0 to 50 p.p.m. rare earths.

Milton, Murata and Knechtel (1944), mainly from the consideration of the formation of weinschenkite, a yttrium-erbium phosphate, postulated that the rare earths of this mineral were initially concentrated by trees. They found 600 p.p.m. rare earths, largely yttria, in the leaves of a chestnut tree growing immediately above the weinschenkite locality near Vesuvius, Virginia, but could not detect any yttria in oak leaves from the same place. Robinson (1943) determined the total rare earths in the leaves of a large number of hickory trees and also in about thirty other kinds of tree leaves growing in several localities where the hickory leaves were highest in rare earths. In general the rare-earth content of other tree leaves was considerably less than that of hickory leaves.

There is no truly quantitative work on the individual rare-earth elements in plants and soils except some spectrochemical determinations of Y and La in soils (Mitchell, 1955). Robinson (1943) made an approximate determination of yttrium in the rare earths in hickory leaves from Rockville, Maryland, by the average-atomic-weight method. He gave the yttria content as 38 wt. per cent, which is in good agreement with the 36 per cent obtained spectrographically on the same sample in the present work.

Rare-earth accumulation and nature of country rock

No detailed analysis has been made of the amount of total rare earths accumulated by hickory trees as a function of the nature of the country rock. However, a brief summary of the available data that bear on this relationship seems appropriate. In the climate of the Eastern United States consistently high amounts (300–2300 p.p.m. of the dry weight of the leaves) are found in areas of granites, gneisses and schists (Robinson and Edgington, 1945). The rare-earth content of leaves of trees in areas of Paleozoic limestones and dolomites ranges only between 100 and 300 p.p.m., whereas in trees from areas of Mesozoic and Cenozoic sands and clays of the Eastern Triassic basins and of the Coastal Plain the rare-earth content is highly variable, 50–800 p.p.m. Part of this wide variation is due to the impossibility of further subdividing this large heterogeneous group according to type of rock with the information at hand. Less than 10 p.p.m. have been found in isolated examples from areas of serpentine, Paleozoic sandstone and a

Tertiary marl. These results suggest that the rare-earth content of hickory leaves, in general, reflects the abundance of these elements in the parent rocks of the soils on which the trees grow. Further work testing this relation should be done, particularly on Coastal Plain localities that yield leaves with several hundred p.p.m. of rare earths.

Method of sampling and locality of samples

It was established by earlier work (Robinson and Edgington, 1945) that the rare-earth content of hickory leaves increases considerably as the season advances, and reaches a maximum late in August or in September in the climate of the Middle Atlantic States. Therefore, the leaves were gathered mostly at the end of the growing season before any browning or other colour change appeared. Whenever possible the smaller trees were bent over and a representative sample (1 kg or more, dried weight) was taken. It had been shown that on two sites small trees in the undergrowth have the same total rare-earth contents as large trees. Botanically the hickory tree samples were *Carya glabra* and *Carya ovalis*. There seems to be no great difference in rare-earth content of the leaves of different kinds of hickory samples on the same small site. In collecting the sample, small and obviously immature leaves were discarded. Hickory has a compound leaf with three to nine leaflets. In stripping a large sample quickly, the petioles and midribs are occasionally left on the twigs, so, for the sake of uniformity, these parts were discarded from all samples. Each sample was dried as rapidly as possible, ground in a Wiley mill and stored in sealed 2 qt glass jars.

Information regarding the localities of the samples has been assembled in Table 1.

Methods of Analysis

Chemical separations

Because direct spectrochemical analysis of the ash of hickory leaves permitted the detection of only a few of the more abundant or spectrochemically sensitive rare-earth elements, it was necessary to separate and concentrate about 20 mg of total rare earths chemically from the leaves in order to determine all the rare-earth elements. A 100 g sample of the dried and ground leaves was ashed in a porcelain dish. Silica was removed by dehydrating with HCl. Any rare earths precipitated with the silica were recovered and added to the main portion. The R_2O_3 group of elements and phosphates were precipitated twice with an excess of ammonia and washed sufficiently to remove the bulk of ammonium chloride.

Phosphorus was then precipitated from a nitric acid solution of the R_2O_3 group by means of ammonium molybdate. The molybdate precipitate was dissolved with ammonia to recover any co-precipitated rare earths. The R_2O_3 group, after being recovered by precipitation with ammonia and dissolution in HCl, was freed of most of the aluminium by pouring the solution into a hot 10 per cent solution of NaOH, and the process repeated.

After another precipitation with ammonia, the R_2O_3 precipitate was dissolved in HCl, the solution evaporated nearly to dryness and taken up in 20 ml of water. The rare-earth elements were then precipitated from this small volume by means of a large excess of oxalic acid. The ammonia and oxalic acid precipitations were

Table 1. Locality and description of hickory leaf (L), soil (S) and water (W) samples

Sample No.	Location	Notes
L-1	50 ft S of Highway 240, 1·2 miles NNW of Rockville, Md.	Composite sample from several trees. Total rare earths found, 2300 p.p.m.
S-1	Same as L-1	Horizon: 0–1 in. Exchangeable rare earths found, 107 p.p.m.
S-2	Same as L-1	Horizon: 0–7 in. Total rare earths found in the clay fraction, 602 p.p.m.
S-3	Same as L-1	Horizon: 38–41 in. Exchangeable rare earths found, 154 p.p.m.
L-2	200 ft SW of corner South Oak and Marshall Sts., Falls Church, Va.	Composite sample from several trees. Total rare earths found, 1000 p.p.m.
W-1	Same as L-2	From a dug well, 40 ft deep. 23 l. processed.
L-3	250 ft NE of corner Meridian and West Sts., Falls Church, Va.	Sample from one tree. Total rare earths found, 1500 p.p.m.
L-4	At foot of 21st St., W. of Highway 29, in White Oak, N.C., a suburb N. of Greensboro.	Composite sample from several trees. Total rare earths found, 1330 p.p.m.
L-5	100 ft N of road, opposite beef cattle barn at Agricultural Research Centre, Beltsville, Md.	Sample from one tree. Total rare earths found, 787 p.p.m.
L-6	Lower edge of Kelley Bank mine, 1 mile ENE of Vesuvius, Va.	Sample from two small trees. Total rare earths found, 220 p.p.m.
L-7	150 ft SE of Highway 11, 5 miles S of Staunton, Va.	Sample from several small trees. Total rare earths found, 288 p.p.m.
S-4	Same as L-7	Horizon: 0–6 in. Exchangeable rare earths found, 75 p.p.m.
W-2	Clifton, Va.	From a dug well. 40 ft deep; 51 l. processed.

repeated if the weight of the ignited oxides considerably exceeded 20 mg or if the colour of the oxides was either too light or too dark.

The exchangeable rare-earth elements were leached out of 250 g samples of soils with 0·05 N HCl in the apparatus described by Schollenberger and Dreibelbis (1930), separated chemically from the other elements in the leachate and determined spectrochemically. The amount in exchangeable form is believed to represent a quarter to a half of the total rare-earth elements in the soils. A 1 N solution of ammonium acetate displaces only a quarter to a third of the amount displaced by 0·05 N HCl (Robinson, 1943).

Spectrochemical analysis

The spectrochemical method used was essentially the method of dilution with pegmatite base (6 quartz, 4 potassium feldspar and 0·1 Fe_2O_3) described by

Gordon and Murata (1952). The rare earths, chemically separated from the leaves and soils, were diluted from 4 to 500-fold with pegmatite base in order to measure the spectral lines of the various elements in the best densitometric range. Analytical curves were established by means of a set of standards containing known amounts of the individual rare earths (spectrochemically pure grade) in pegmatite base. The precision and accuracy of the determinations are within ± 10 per cent of mean values reported. Summations for total rare earths ranged from 92 to 110 per cent. The small quantities of the separated rare earths available precluded the use of the more accurate spectrochemical method (± 5 per cent) described by Rose *et al.* (1954).

The following spectral lines (in ångstrom units) were used for the determination of the individual rare-earth elements.

Y	3173·052	3195·615	3242·280
La	3104·589	3245·120	3337·488
Ce	3201·714	3243·370	
Pr	3245·462		
Nd	3134·897	3328·270	
Sm	3408·668		
Eu	2813·95	2906·676	
Gd	3032·850	3331·3188	3350·482
Tb	3293·07	3324·40	
Dy	3319·887	3407·80	3169·978
Ho	3474·25		
Er	3220·730	3230·585	
Tm	3131·26	3362·61	
Yb	2970·564	3289·37	
Lu	2911·39	3359·56	

Analytical Results

General aspects

The results of the analyses are given in atomic percentages of total rare-earth elements in Tables 2 and 3. Certain general aspects of the assemblages of elements found in both the leaves and soils may be first noted. Four elements, Y, La, Ce, and Nd, constitute 80–91 at. per cent of the total rare-earth elements. The high proportion of yttrium relative to the three cerium-earth elements indicates that at least two separate assemblages are involved, one rich in yttrium group, and the other in cerium group. The existence of a separate cerium-earth assemblage in some soils that are derived from granites and crystalline schists is indicated directly by residual monazite crystals that can be obtained by panning these soils. The recent study by Silver and Grunenfelder* of the weathering of allanite in granites of northern Georgia suggests that allanite could be a major source of available cerium-earth elements in soils derived from some granites.

* L. T. Silver and Marc Grunenfelder, Alteration of accessory allanite in granites of the Elberton area, Georgia. Abstract in programme of the 1957 meeting of Geol. Soc. Amer. p. 126, (1957).

The percentages of cerium relative to other elements of its group, such as La and Nd, is abnormally low in leaf samples L-1 to L-6 and in soil sample S-3. These abnormally low proportions of cerium in its group will be discussed in detail in a later section.

Table 2. Composition in atomic per cent of total rare-earth elements separated from hickory leaves

	L-1	L-2	L-3	L-4	L-5	L-6	L-7	Average
Y	42	38	34	34	23	55	24	36
La	16	15	20	13	16	9	23	16
Ce	6	7	7	12	21	11	31	14
Pr	0·9	1·6	2·1	1·8	3·7	0·8	1·9	1·8
Nd	18	25	22	26	23	12	13	20
Pm	—	—	—	—	—	—	—	—
Sm	3·2	1·0	1·1	1·0	1·2	1·5	0·8	1·4
Eu	0·9	0·8	0·9	1·1	0·8	0·4	0·4	0·8
Gd	3·5	3·3	3·6	3·2	3·8	2·4	2·0	3·1
Tb	0·7	0·7	0·7	0·7	0·7	0·4	0·2	0·6
Dy	3·1	2·7	2·7	2·7	2·2	3·2	1·7	2·4
Ho	0·9	0·6	0·8	0·7	0·7	0·9	0·6	0·7
Er	2·2	2·5	3·1	2·6	3·4	1·9	0·8	2·4
Tm	0·3	0·2	0·3	0·2	0·2	0·3	0·1	0·2
Yb	1·7	1·3	1·2	1·1	0·5	1·5	0·4	1·1
Lu	0·2	0·2	0·2	0·2	0·1	0·2	0·1	0·2

Table 3. Composition in at. per cent of exchangeable rare-earth elements separated from three soils and of total rare-earth elements from a soil clay, with other data for comparison

	S-1	S-3	S-4	S-2 (clay)	Shales (Minami, 1935)	Igneous rocks (Sahama and Vähätalo, 1941)
Y	23	37	20	20	28	27
La	16	14	13	22	12	13
Ce	32	8	38	18	29	25
Pr	2·7	1·7	3·1	2·4	3·5	5
Nd	15	21	15	24	14	14
Pm	—	—	—	—	—	—
Sm	1·6	2·2	1·7	4·4	3·7	4·0
Eu	0·6	1·0	0·6	1·0	0·6	0·6
Gd	2·4	3·9	2·6	2·7	3·5	4·2
Tb	0·6	0·9	0·6	0·7	0·5	0·6
Dy	2·7	3·9	2·9	1·8	2·4	2·4
Ho	0·7	0·8	0·6	0·6	0·6	0·6
Er	1·5	2·5	1·2	0·9	1·3	1·6
Tm	0·3	0·3	0·2	0·1	0·1	0·3
Yb	1·0	1·5	0·6	0·6	1·3	1·3
Lu	0·1	0·2	0·1	0·1	0·4	0·6

The yttrium group (arbitrarily defined to include yttrium and the lanthanide elements from Tb to Lu) make up 25–63 at. per cent of the total. Yttrium, as usual, is the dominant element and constitutes 75–87 per cent of the group. The absence of any pronounced maximum in the abundance of elements from Tb to Lu in all samples shows that the yttrium group most closely resembles the yttrofluorite type of complete assemblage as defined by GOLDSCHMIDT and THOMASSEN (1924). As no discrete yttrium-earth mineral has been recognized in the soils, the

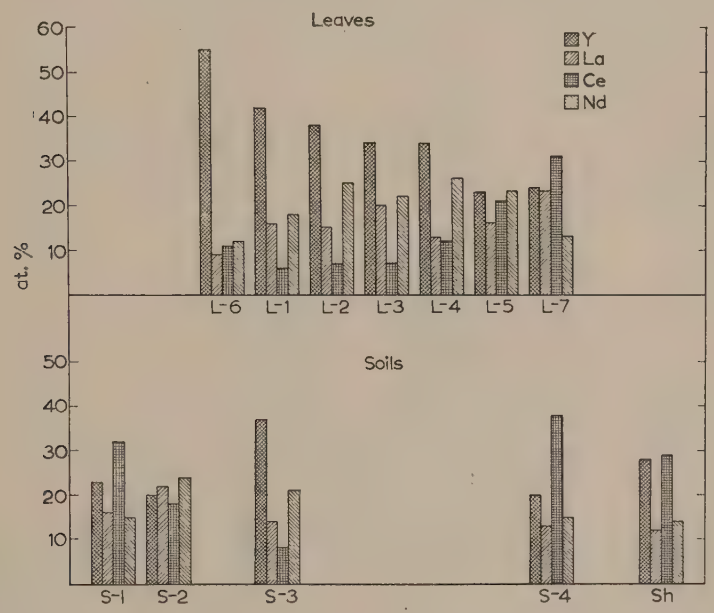

Fig. 1. Diagrammatic representation of the concentrations of the major rare-earth elements, Y, La, Ce, and Nd (at. per cent of total rare-earth elements) in leaves, related soils, and in average shale, Sh.

source of the yttrium-earth elements is presumed to be apatite, garnet, calcite and other easily weathered minerals that were original constituents of the parent rocks of the soils.

The four major elements in each sample, Y, La, Ce and Nd, have been plotted in Fig. 1; the order of the leaf samples from left to right in the figure is, in general, according to decreasing atomic percentage of yttrium. The manner in which the composition is determined primarily by the relative proportions of yttrium and cerium groups is clearly evident. At one end of the range of variation, sample L-6 contains 55 per cent yttrium and a combined percentage of La, Ce and Nd of 32, whereas at the other end, Sample L-7 has 24 per cent yttrium and a combined percentage of the cerium-earth trio of 67.

The previously mentioned low percentages of cerium in most of the samples are also well shown and can be contrasted with the high percentage found in a normal assemblage, as exemplified by MINAMI's average for European and Japanese shales labelled Sh in the figure.

Variations of cerium

The large variation and abnormally low concentrations of cerium with respect to other members of the cerium group are the most striking features of the assemblages in both leaf and soil samples. In cerium-earth minerals such as monazite and allanite (Vainshtein *et al.*, 1956; Murata *et al.*, 1957), in igneous rocks

Table 4. Proportions of cerium in leaf and soil samples and in comparison materials

Material	Nature of rare earth	Ce/(La + Nd)
Igneous rocks	Total	0·94 (0·78 to 1·39)
Shales	Total	1·12 (0·78 to 1·46)
Cerium minerals	Total	1·09 (0·84 to 1·41)
Leaves		
L-7	Total	0·86
L-5	Total	0·54
L-6	Total	0·52
L-4	Total	0·31
L-1	Total	0·18
L-2	Total	0·18
L-3	Total	0·16
Rhabdophane (Conn.)	Total	0·01
Soils		
S-4	Exchangeable	1·36
S-1	Exchangeable	1·03
S-2 (clay)	Total	0·39
S-3	Exchangeable	0·23

(Sahama and Vähätalo, 1941), and in shales (Minami, 1935), cerium is the most abundant element of its group, commonly equalling or exceeding the combined percentages of La and Nd. As shown in Table 4, the atomic ratio Ce/(La + Nd) for these materials varies between 0·8 and 1·5 and the general average is 1·0. Among our materials, leaf sample L-7 and topsoils S-1 and S-4 are the only samples whose ratios fall in this normal range.

The deviations from normal ratios are all in one direction, that is, all deviant leaf and soil samples have subnormal ratios. The extremely low value found in the rare mineral rhabdophane from Connecticut (Hildebrand, Carron and Rose, personal communication, 1957) is included in Table 4 because this mineral very likely formed in the zone of weathering and biological accumulation may have been a factor in its formation. The low ratios clearly indicate that cerium has been separated from the other elements of its group. In the soil samples, there could be an actual dearth of cerium or, more likely, a substantial part of the total cerium could be in a form not extracted by ion-exchange solutions or by hickory trees.

In contrast to the other elements of its group, cerium readily undergoes a valence change from 3^+ to 4^+ within the range of pH prevalent in soils. The chemical properties of quadrivalent cerium differ markedly from those of trivalent

rare earths so that this oxidation reaction provides a simple way of separating cerium from the others. That a precipitate of cerous hydroxide is rapidly oxidized by air to ceric hydroxide is a well known fact in analytical chemistry, and forms the basis for separating cerium on an industrial scale (Powell, 1939). Quadrivalent cerium could become fixed in a soil by precipitation or co-precipitation as a highly insoluble compound or by being held tenaciously in ion-exchanging materials of the soil. So fixed, the element would not be available to the hickory tree nor would it be extracted by the usual ion-exchanging solutions.

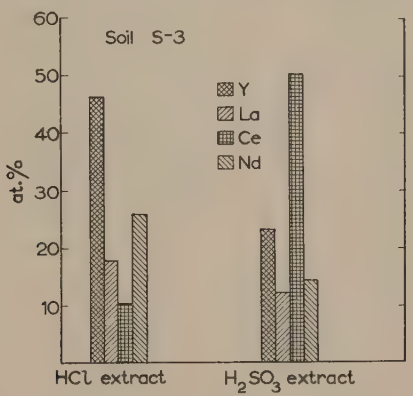

Fig. 2. Diagrammatic representation of the concentrations of the major rare-earth elements (at. per cent of total Y, La, Ce, and Nd) extracted from a subsoil sample by dilute HCl and by dilute H_2SO_3.

We arrive at the interesting conclusion that the cerium in soils remains trivalent and maintains its normal abundance among the suite of available rare-earth elements only in a reducing environment where the concentration of free oxygen is very low. The three samples from the soil profile at Rockville, Maryland, provide a striking confirmation of this inference. It must be remembered that the content of free oxygen in a well-drained soil profile is not a function of proximity to the surface but rather of the amount of oxidizable organic matter present (Merkle, 1955). Sample S-1 representing the top inch of mineral soil just below the leaf mold shows the normal abundance of cerium among the available rare-earth elements and contains 19 per cent organic matter. In contrast, Sample S-3 from a depth of 40 in. shows an abnormally low proportion of available cerium and contains only 0·19 per cent organic matter. Sample S-2 is not directly comparable with the other two because its rare-earth elements represent the total that was present in the clay fraction* separated from the top 7 in. of the profile, but it does show an intermediate proportion of cerium. Sample S-4 from near Staunton, Virginia, represents the top 6 in. of a shallow residual soil over limestone. Here again a normal proportion of available cerium, Ce/(La + Nd) = 1·36, correlates with a high content of organic matter of 11 per cent.

Further information on the valence of cerium in subsoil Sample S-3 was

* E. J. Pedersen, U.S. Department of Agriculture, kindly made the mechanical separations of the fractions.

obtained by substituting 0·05 N H_2SO_3 for 0·05 N HCl in the procedure for determining the exchangeable cations. Besides providing requisite hydrogen ions for displacing the exchangeable cations of the soil, sulphurous acid was expected to reduce any quadrivalent cerium that might be present and thereby convert it to an extractable form. The results of the experiment are shown in Fig. 2. Only the four major elements, Y, La, Ce and Nd, were determined in the extract so the results are expressed in terms of atomic per cent of the total of the four elements. The total rare earths extracted by 0·05 N H_2SO_3 corresponds to 83 p.p.m. of the soil sample compared to 152 p.p.m. extracted by 0·05 N HCl.

It is apparent in Fig. 2 that sulphurous acid has produced a very striking increase in the proportion of extractable cerium. This increase is a strong indication that much of the cerium in the sample is quadrivalent and becomes available only through chemical reduction to the trivalent state. Relative to the other rare-earth elements, so much cerium has been extracted by sulphurous acid that the ratio Ce/(La + Nd) attains an abnormally high value of 1·90, which suggests that cerium may actually be accumulating in the subsoil. The other elements, Y, La and Nd, which do not undergo any change in valence, show no essential difference in relative proportions to one another in the dilute HCl and H_2SO_3 extracts.

Thus, the results of our preliminary study of available rare earths in soils are in good agreement with the concept that cerium can retain its trivalency only in a reducing environment and becomes quadrivalent and less available in an oxidizing environment. In this respect cerium resembles iron and manganese which also require a reducing environment for their lower valence. Work is in progress on other soil samples in order to check these relations further.

Question of Biological Fractionation

The roots of hickory trees are known to penetrate deeply into the soil, and in regions of deep weathering they extend well into the underlying saprolite. The abnormally low cerium content in six of the seven leaf samples indicates that hickory trees feed mostly in horizons where available cerium is low, namely, in the subsoil. Thus the nature of the root system and the proportions of rare-earth elements assimilated by the hickory tree both attest to its habit of feeding deep in the soil profile, especially during seasons when the surface soil is dry.

Samples S-1 and S-3 (Fig. 1) show how the assemblages of available rare-earth elements can differ between the topsoil and the subsoil in a single profile. In addition to the great contrast in the proportion of cerium, there is a moderate difference in the proportions of yttrium and cerium groups. In the face of this variability, the resemblance of the assemblage in leaf sample L-1 to that in the subsoil Sample S-3 is remarkably close. If it is assumed that Sample S-3 represents the entire subsoil being exploited by the hickory tree, the striking resemblance in composition could be interpreted to mean that the tree has little power of discrimination and takes up the rare-earth elements substantially in the proportions that they are available in the subsoil.

Soil S-4 at the Staunton, Virginia, locality is very rocky and shallow, and except for the surface layer of leaf mould shows no clear development of a profile.

The shallowness of the soil apparently has forced the hickory trees to feed mostly in the top soil and this may explain why leaf sample L-7 has the highest proportion of cerium among all of the leaves. There is a notable difference in the proportion of lanthanum between the leaf sample and the surface soil S-4 which is as yet unexplainable but may possibly be due to the alkalinity induced in a part of the soil by the underlying limestone. The proportions of other major elements, Y, Ce, and Nd, are similar, which again suggests that the rare-earth elements taken up by hickory trees are substantially those in available form in the soil. It is on the basis of this limited evidence obtained on samples from two localities that we conclude tentatively that the hickory trees do not materially fractionate these elements. The data might be interpreted as showing a slight enrichment of the yttrium group of elements in the leaves relative to the soil, but such a fine detail cannot be resolved with certainty at present.

A study of the complete analyses of Tables 2 and 3, in general, supports the prevailing idea of the coherence of the trivalent rare-earth elements, but there are notable deviations. Unexplainable at present are appreciable variations in the ratio of yttrium to the other yttrium earths, of erbium to ytterbium (Sample L-5), and of other pairs of elements close together in the lanthanide series. Elements in the middle of the series, say from europium to dysprosium, have the complication that they may be contributed by sources of either yttrium or cerium groups. A search has been made for variations in europium which could be attributed to its easy reduction to the divalent state (Goldschmidt, 1954), with negative results.

In recent years, very rapid separations of the individual rare-earth elements have been achieved by ion-exchange techniques involving elutriation with organic chelating agents (Spedding *et al.*, 1951). Because soils contain both ion-exchanging substances and organic chelating compounds, possibly some fractionation might occur perhaps seasonally in soils through ion-exchange processes, but at present, such an effect remains undetected.

Rare-earth elements in ground waters

A preliminary study has been made of the rare-earth elements in ground water by analysing samples from two dug wells in the Virginia Piedmont area of crystalline schists, west of Washington, D.C. (Table 1). Both samples contained less than 50 p.p.m. of total solids. In spite of evaporating large volumes of samples and chemically concentrating the rare-earth elements, we recovered such small amounts that only the more abundant or spectrochemically sensitive elements could be determined. The results are tabulated below (Table 5).

From these partial analyses, the content of total rare-earth elements in W-1 and W-2 are estimated to be about 2 and 60 p.p.b. respectively. The relative amounts of the elements fall in the range found in leaves and soils except for the unusually low proportion of neodymium in W-2. Sample W-2 also shows the low proportion of cerium [Ce/(La + Nd) = 0·04] previously noted in leaves and subsoils.

These results indicate the kind and amount of rare-earth elements being transported by local ground waters. It has been estimated that as much as 1000 lb of transpired water are required to produce a pound of dry matter in tree growth

Table 5.

	W-1 (Falls Church)	W-2 (Clifton)
	(parts per billion)	
Y	0·8	41
La	0·4	12
Ce	—	0·5
Pr	—	—
Nd	—	0·7
Sm	—	—
Eu	—	—
Gd	—	—
Tb	—	—
Dy	—	0·7
Ho	—	—
Er	—	0·8
Tm	—	0·3
Yb	0·03	1·6
Lu	—	0·3

(*U.S. Dept. Agriculture Yearbook for* 1949, *Trees*). Thus the leaves of a tree transpiring water with the composition of the Clifton wellwater could accumulate about 60 p.p.m. of total rare earths. Leaves of hickory trees growing near the Clifton well have ten times this concentration.

Recent laboratory studies of water solutions of many elements including some of the rare-earth elements, at concentrations of 10^{-8} M and less and with pH higher than 3, have shown that the elements are not present as simple ions but as some kind of quasicolloidal aggregates that can be separated through dialysis and sedimentation (Schweitzer and Jackson, 1952). The addition of acids, electroytes or complexing agents to these extremely dilute solutions reduces the proportion of rare-earth elements present in the quasi-colloidal form. If the rare-earth elements occur at the determined concentrations of 10^{-7} to 10^{-11} M as quasi-colloids in ground waters they probably would be filtered or sedimented out of solution as the waters moved through soil and saprolite. Very likely the greater part of the rare-earth elements are held in solution by the complexing action of various organic substances present in ground waters. This possibility, in turn, would raise the question of the form in which these elements are assimilated by plants.

It is obvious that this preliminary study has clarified only the more gross aspects of the biogeochemistry of the rare-earth elements, such as the redox reaction of cerium in soils, and work is being continued to elaborate and refine the data.

Acknowledgements—Acknowledgement is made to L. T. Alexander, U.S. Department of Agriculture, for the loan of special apparatus and advice on the collection of soils. We are also indebted to a number of colleagues in the U.S. Geological Survey for assistance and advice. H. J. Rose, Jr., analysed several of the leaf samples spectrochemically and M. K. Carron

confirmed the low proportion of cerium in one of the leaf samples chemically. Help with the analysis of the water samples was provided by L. L. Thatcher and H. Levine.

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Analyses of the standard rocks G1 and W1

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Abstract—Spectrographic determinations, by a method based on successive additions, are reported for cobalt, copper, gallium, manganese, molybdenum, nickel, vanadium and zirconium in the standard rocks G1 and W1.

The evaluation of probable values for the true concentrations from available results is discussed.

1. Introduction

Analytical results for the standard rock samples, granite G1 and diabase W1 (Fairbairn *et al.*, 1951), obtained by optical spectrography (Ahrens, 1954; Turekian *et al.*, 1957), fluorescent X-ray spectrography (Hower and Fancher, 1957), mass spectrometry (Herzog and Pinson, 1955), neutron activation (Smales, 1955; Smales *et al.*, 1955), polarography (Smythe and Gatehouse, 1955) and various chemical methods (Ahrens, 1954; Fairbairn *et al.*, 1951; Degenhardt, 1957), show clearly that accurate values for the elements present at low concentrations will be obtainable only on the basis of a large number of independent analyses. Although published results for a few elements do show a tendency to cluster about a moderately well-defined value, those for other elements are scattered haphazardly over ranges of which the upper limits are several times as great as the lower limits. For the latter elements, a mean of a small number of results, whether arithmetic or geometric, has little significance; this is clearly demonstrated by the series of results obtained for rubidium (Ahrens, 1954; Hower and Fancher, 1957; Herzog and Pinson, 1955).

It is therefore desirable that every result obtained for these samples should be published and taken into consideration if spectrographers are to secure their objective of standard rock samples with accurately known concentrations of the elements of interest. This is the main reason for submitting the results for cobalt, copper, gallium, manganese, molybdenum, nickel, vanadium, and zirconium that were obtained in this laboratory. A subsidiary reason is to illustrate the performance of a quantitative spectrographic procedure based on successive additions and with no internal standard.

2. Experimental

Two additions were made to each sample, one approximately equal to, and the other approximately twice the estimated original concentrations of the elements added. The original concentrations were determined by solving pairs of equations of the type

$$\log C = A + \log I$$

(where C denotes concentration, I line intensity, and A a constant) first for A and then for $\log C$.

For any one analysis line, the values for A obtained with the smaller and larger additions generally differ a little as a result of errors in the determination of $\log I$. Differences are also produced by self-absorption of, and by one type of interference with, the analysis line; these

two factors are distinguishable by the algebraic sign of the difference produced. A line for which the two values for A do not differ significantly is used in the actual determination of $\log C$.

All analyses were made by each of two operators who worked independently except that they used equivalent additions.

The agreement of replicates was only fair for some elements with sample G1; this sample behaved somewhat erratically during excitation. No attempt, however, was made to modify the conditions of excitation because one object was to test the performance of the method in its general form, as applied to any unknown sample of mineral powder.

3. Results

The mean values obtained for the concentrations of the eight elements are recorded in Table 1; they also appear in the dot frequency diagrams of Fig. 1,

Table 1. Analytical results (p.p.m.) for G1 and W1

Element	G1	W1
Cobalt	<2	45
Copper	15	135
Gallium	23	23
Manganese	190	1450
Molybdenum	7	5
Nickel	<2	85
Vanadium	38	310
Zirconium	230	150

together with all available results for these elements. These diagrams show clearly that the accuracy of results obtainable by a general method based on successive additions, without an internal standard, is on the whole at least as high as that obtainable by the more conventional methods.

As two independent sets of analyses were made, the precision of the mean values could be calculated. The coefficient of variation for the mean value was found to be 10 per cent, based on 14 degrees of freedom. (This measure of precision is not comparable with those usually quoted because it covers additional sources of variation—variation between operators, for example.)

In general, results obtained by a method based on successive additions may be subject to systematic errors from two main sources. One source is the difference in spectrographic behaviour between the compound added and that originally in the sample. Experience has shown that errors from this source are negligible, provided that the compound to be added is carefully selected. In doubtful cases the additions may be repeated with a different compound.

The other source of systematic error is self-absorption of the analysis line; these errors are necessarily positive. Although the constant A responds markedly to serious self-absorption, it is only where a weaker analysis line is available that it is possible to determine whether a moderate difference in the two values for A is due solely to experimental error. In other cases it must be assumed that slight self-absorption may have occurred and that the result may be in error.

Although both results for gallium and for vanadium appear to be high (see Fig. 1), it is improbable that they have serious systematic errors from either source.

Vanadium was added both as a compound in solution and a different compound incorporated as a solid, and both additions gave the same result within experimental error. Analysis lines of very different intensities also yielded the same result for sample W1. This result, 310 p.p.m., was later verified by an absolute method of fluorescent X-ray spectrography which yielded the value 320 p.p.m. As the concentration of vanadium is much lower in G1, it is unlikely that the result for this sample is in error due to self-absorption of the analysis line.

The results for gallium could not be checked by using different additions and analysis lines of very different intensities. However, these results, 23 p.p.m. for each sample, were verified by the X-ray method which yielded 20 p.p.m. for G1 and 24 p.p.m. for W1; the pairs of results agree within experimental error (about ± 10 per cent for each method).

Although the result for zirconium in sample G1 falls near the mean of previous results, that for W1 is well removed from the cluster formed by the great majority of previous results (Fig. 1). Analyses by the X-ray method yielded 213 p.p.m. for G1 and 98 p.p.m. for W1. The latter value falls inside the cluster of previous results, and it must be concluded that the authors' result for W1 is seriously in error. The most plausible cause of this error is that the background correction was impaired by the nature of the background about the analysis line. This is a source of error that exists wherever line and background are of comparable intensities and for which there is no remedy.

All available evidence showed that the results in Table 1, except that for zirconium in sample W1, are probably free from serious systematic error. The measure of precision ± 10 per cent may therefore be taken as a passably good measure of accuracy.

4. Evaluation of Probable Values for True Concentrations

Fig. 1 illustrates the marked differences between determinations for any one element. These differences are generally so great that they cannot be attributed solely to lack of precision in the individual values. For example, if the results for copper in G1 are treated as replicates, then the standard deviation for a single result is 5·4 p.p.m., or 42 per cent of the mean. There is no doubt that all analysts involved could produce evidence to show that the coefficients of variation of their results were very much less than 42 per cent. It is thus apparent that quite large systematic errors are associated with many of the results.

Where few values are available, nearly all of which were obtained by one method of analysis, fortuitous cancellation of systematic errors is unlikely. Examples in Fig. 1 are the results for gallium and vanadium. In such cases, a mean of all values may have a large systematic error; one of the extreme values may later be shown to be the most accurate.

On the other hand, if the results tend to cluster and were obtained by really independent methods, almost complete cancellation of systematic errors may be assumed because it is very unlikely that the independent results have similar systematic errors. For example, both dot frequency diagrams for nickel (Fig. 1) show a well-defined cluster of values obtained by optical spectrography, neutron activation, polarography and a chemical method. There is little doubt that the

true concentration of nickel in each sample is located within the respective cluster of values. One may also discard, with some confidence, those extreme values that are well separated from a cluster.

Whether the results are scattered or clustered, the arithmetic mean must be used as the probable value for the true concentration because the systematic errors

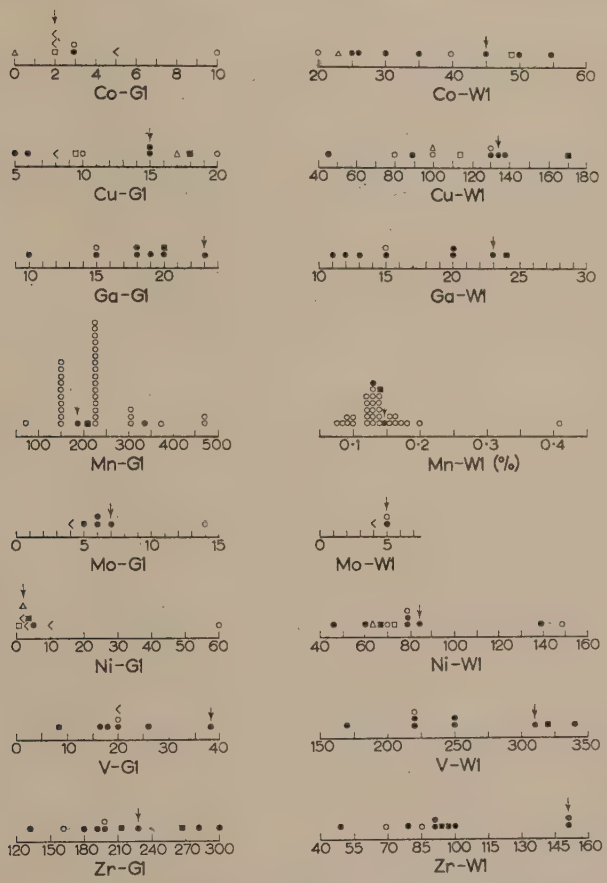

Fig. 1. Dot frequency diagrams of available results; ● optical spectrography; ■ fluorescent X-ray spectrography; ○ chemical methods; □ neutron activation; △ polarography; < less than, placed at limit (optical spectrography). Authors' results are indicated by arrow over symbol.

are nearly always quite unknown. This involves the assumption that positive and negative systematic errors of the same magnitude are equally likely. Use of the geometric mean involves the assumption that the positive systematic errors have the greater magnitude, and this is quite unwarranted.

A further assumption, that the systematic errors associated with a set of independent results may be included with the random errors, permits the calculation of a confidence interval for the mean. However, such an interval must be treated with caution, particularly where most of the results were obtained by one method of analysis.

The probable values and confidence intervals given in Table 2 were obtained as follows. The intervals are 90 per cent confidence intervals; that is, on the assumption made, the odds are 9 : 1 that the true concentration lies within this interval. (On the average, these intervals are 1·8 times as great as those given by the standard deviations of the means.) All results were used for cobalt (W1), copper, gallium, molybdenum, vanadium, and zirconium (G1). Extreme values, well removed from clusters containing results obtained by at least three different methods, were discarded for cobalt (G1—10 p.p.m.), manganese (G1—two at 460 p.p.m.; W1—0·41 per cent), nickel (G1—60 p.p.m.; W1—140 and 150 p.p.m.), and zirconium (W1—two at 150 p.p.m.). Statistical evidence was also used in the selection of these values, but this evidence is weakened by the inclusion of systematic errors with random errors. Only an order of magnitude without a confidence interval is given where very few results are available.

Table 2. Probable concentrations (p.p.m.) and 90 per cent confidence intervals

Element	G1	W1
Cobalt	~2	36 ± 7
Copper	13 ± 3	112 ± 19
Gallium*	18 ± 2	17 ± 3
Manganese	217 ± 18	1330 ± 81
Molybdenum	~7	~5
Nickel	~2	71 ± 7
Vanadium*	21 ± 7	255 ± 35
Zirconium	214 ± 28	84 ± 10

* The true values probably lie near, or a little beyond, the upper limits.

Table 2 shows clearly that none of the concentrations is yet known with the accuracy required for standard samples. This is so despite the fact that all assumptions on which the table is based tend to produce the most favourable outcome.

Acknowledgement—Dr. K. Norrish, of the Division of Soils, C.S.I.R.O., kindly made available the values for gallium, vanadium and zirconium, as determined by fluorescent X-ray spectrography, that are recorded in Section 3 and also appear in Fig. 1.

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A chemical and petrographic study of Pre-Cambrian sediments

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Abstract—Over ninety Pre-Cambrian argillaceous rocks (mainly Canadian greywackes, argillites and a few low-grade schists) were studied petrographically and analysed spectrochemically for the following trace elements: B, Cr, V, Ni, Cu, Mn and Ba.

The petrographic study indicated that greywackes are argillaceous sandstones, commonly with a microbreccia texture, as pointed out in several recent papers and textbooks, rather than, as often held, the basic equivalent of an arkose, consisting largely of relatively undecomposed particles of basic igneous rocks or their metamorphosed equivalents. Only volcanic greywackes approach the latter definition.

The trace element composition of the greywackes and argillites suggests that they are marine rather than freshwater deposits. It also suggests that the oldest sediments yet recognized in the Pre-Cambrian were accumulated in waters which differed little in composition from the seas of the present day.

The trace element content of the Pre-Cambrian argillaceous rocks appears to be normally distributed (statistically), and is similar for Archean and Proterozoic as well as later rocks.

The range in composition for any element extends from zero to about twice its mean value. The probability that a rock will violate this distribution law is small.

Introduction

Statement of problem

The primary purpose of this investigation was to determine the amounts of a selected group of trace elements in greywackes and argillites from a number of Pre-Cambrian series. To the writer's knowledge this is the first study of this type, concerned with Canadian Pre-Cambrian sediments, and for this reason has been carried out on an extensive rather than intensive scale. The following considerations prompted the investigation:

(1) Investigations by Landergren (1945) lead to the conclusion that marine sediments may be distinguished from non-marine by their higher boron content. Does the boron content indicate that Pre-Cambrian sediments were deposited in marine waters and was the salinity of these waters comparable with that of the present-day oceans?

(2) Does the contents of elements such as nickel, chromium, support the derivation of greywackes from mechanically weathered basic terrains?

(3) Are there significant differences in the boron or other trace elements in sediments of similar lithology but widely differing age?

Most of the rocks studied were collected from the following main regions in the provinces of Ontario and Quebec: Cadillac-Malartic area, Kirkland Lake-Timmins area, Cobalt-Bryce-Robillard area, north shore of Lake Huron and the Lake Nipigon area. A few specimens were collected from Labrador and Finland.

In eastern Canada most of these fine-grained greywackes, argillites and low-grade schists belong to the Keewatin, Timiskaming, Huronian, Animikie and Keweenawan series. The Keewatin and Timiskaming sedimentary rocks belong to the earliest part of the Pre-Cambrian (Archean) but are locally separated from one another by an unconformity: the Huronian, Animikie and Keweenawan occur in the younger Pre-Cambrian (Proterozoic).

All the specimens analysed were examined petrographically. Particular attention

was given to the petrography of the greywackes, in order to assess the validity of concepts developed in the valuable contributions of Bailey (1930, 1936), Tyrrell (1933), Pettijohn (1943, 1949, 1950), Eskola (1932) and Simonen (1953).

Petrology

Definition and classification of greywacke

There has been much controversy regarding the definition of greywacke. Twenhofel (1950) defines greywacke as the basic equivalent of arkose having a large content of little-decomposed particles derived from basic igneous rocks or their metamorphosed equivalents. There should be a large content of ferromagnesian minerals and soda-lime feldspars. Pettijohn (1949) objects to this definition stating that "study of many specimens and published descriptions of greywacke leads to the conclusion that detrital ferromagnesian minerals are rarely, if ever, a normal constituent of that rock." In general, greywacke may be defined as an impure sandstone resembling a microbreccia. According to Gilbert (Williams, Turner and Gilbert, 1954) "they are aggregates of sharply angular fragments of every size between sand and fine gravel and impalpable fragments. They are sandy or gritty, but choked with argillaceous matrix, and hence have particularly low permeability. Some greywackes contain so much argillaceous material that their larger grains are clearly separated in it and appear to be suspended in it, and these grade by all stages into rocks, usually called sandy or silty mudstones, shales and argillites, in which grains of sand and coarse silt constitute only a small part of the whole aggregate."

The greywackes studied were classified according to a system essentially the same as Gilbert's (Williams, Turner and Gilbert, 1954). Gilbert recognizes two general varieties of greywacke, chiefly reflecting differences in the source rocks. The first group, containing more feldspar than rock fragments, is known as arkosic greywacke if the feldspar content exceeds 25 per cent, or feldspathic greywacke if between 10 and 25 per cent. The second type, containing abundant rock fragments, is called lithic greywacke, and may be further subdivided, depending on whether the fragments are volcanic (volcanic greywackes), or schist (schist greywackes) etc. Quartz greywackes, in which the grains are largely quartz and chert, while feldspars and unstable rock fragments constitute less than 10 per cent each, represent more through weathering prior to deposition. From the above considerations, it is evident that the presence of abundant dark coloured rock fragments, though typical of lithic greywackes, is not an essential characteristic of all greywackes, as here defined.

From the material investigated, and from a review of the Canadian literature, the writer concludes that arkosic greywackes are the commonest of Canadian greywackes. Quartz is usually an abundant constituent of Pre-Cambrian greywackes from all levels of the Pre-Cambrian.

Pre-Cambrian greywackes and their origin

Pettijohn (1943) has presented an interesting analysis of this problem as it applies to Archean greywackes in western Ontario, and in general the present study has substantiated his observations

The Archean ("Timiskaming") greywackes are associated with conglomerates, arkoses and volcanics, particularly tuffs. Younger Pre-Cambrian greywackes are also found and these are interbedded locally with quartzites and arkosic quartzites. The conglomerates in most cases are polymict, the pebbles including sedimentary and schist fragments, volcanic fragments and granite, porphyry, and diorite. Usually volcanic, plutonic or sedimentary fragments will predominate in particular outcrops or beds. Gradations from one type of lithology to another are often found in greywacke sequences, so that entire formations or series are described as "greywacke-slate" or "slate-conglomerate" in the older reports.

Sedimentary structures are typical of those reported from other greywacke occurrences. Bedding may be absent but is usually well developed sometimes on so small a scale as to be termed "varved" bedding. Graded bedding is characteristic but is not always present. Cross-bedding has been observed locally, but is usually on a small scale and confined to individual beds. Ripple marks are uncommon, but have been reported from the Kirkland Lake area. Slump structures are found locally. The greywackes, for the most part, constitute sedimentary successions totalling thousands of feet in thickness, or are portions of thick successions.

As has been pointed out by several authors in recent years, the angular character of the sand-size grains in greywackes and the mixed character of the sediment, as well as the scarcity of strong cross-bedding, ripple marks and other indications of wave and current action, indicate that the greywackes were deposited with a minimum of working and reworking by the agencies mentioned. The graded bedding has been attributed (a) to fractionation by settling of rapidly accumulating mixed sediment through still water, (b) to sorting by the action of turbidity currents Kuenen and Migliorini (1950). Such conditions were probably afforded by deep "eugeosynclinal" troughs or volcanic island arcs on the continental borders.

The granite boulders in the conglomerates and the quartz and feldspar grains in the greywackes indicate that even in the Archean, acid plutonic rocks and gneisses were available as sources of the sediment. It must be recognized, of course, that quartz and feldspar grains may also have come in part from volcanic rocks, such as quart porphyries and dacite. This has been demonstrated in the Kirkland Lake area, for instance, by Hewitt (1949). Chemical evidence also supports the view that the products of mainly mechanical weathering of normal crustal rocks have contributed largely to the formation of greywackes and that they cannot be regarded as the result of mechanical weathering of basic rocks (see analyses 1 and 2, Table 1). Thus the high silica, low magnesium, iron and calcium are incompatible with the older conception. In effect, except for the low potassium, analysis 1 (Timiskaming greywacke) is not far from average granite. It seems likely that these sediments must have been derived from rather sodic granites or rhyolites, or both. Plutonic and volcanic rocks of this character are found in the area.

Spectrochemistry

General

The Pre-Cambrian argillites and greywackes were analysed spectrochemically (each sample at least twice) in order to determine their content of B, Cr, V, Ni, Cu,

Table 1. Chemical composition of four Pre-Cambrian sediments*

	(1)	(2)	(3)	(4)
SiO_2	70·0	61·0	63·0	58·9
TiO_2	0·6	0·4	0·4	0·4
Al_2O_3	13·2	18·0	12·1	17·6
Fe_2O_3	1·0	1·2	0·4	1·8
FeO	3·9	4·6	2·7	5·7
MnO	0·1	0·1	0·1	0·1
MgO	2·9	4·0	3·6	4·5
CaO	0·7	1·4	6·7	1·6
Na_2O	4·0	3·2	2·7	4·3
K_2O	1·2	2·3	2·9	2·4
H_2O^+	2·0	3·6	1·5	2·7
H_2O^-	0·1	0·1	tr.	0·2
P_2O_5	—	tr.	tr.	tr.
CO_2	—	—	3·5	—
C	tr.	—	—	—
S	—	—	—	—
Total	99·7	99·9	99·6	100·2

* Figures corrected to one decimal place.

(1) Timiskaming greywacke, near Porcupine Lake, Ontario; H. B. Wiik, analyst.
(2) Timiskaming argillite, Ogden Township, Ontario; H. B. Wiik, analyst.
(3) Bruce argillite, Lake Penage, Ontario; H. B. Wiik, analyst.
(4) Keweenawan argillite, Batchawana Bay, Ontario; H. B. Wiik, analyst.

Mn and Ba. Reconnaissance qualitative analyses were run on some forty samples in order to ascertain the general content of trace and major oxides. Such information aided in developing a suitable matrix from which standards could be made.

Standards were prepared from Johnson-Matthey "Specpure" oxides of the metals mixed with an arbitrary "greywacke-argillite like" matrix. The matrix used was prepared by mixing very pure natural quartz with spectrochemically pure chemicals in proportion to the following analyses: SiO_2 (66·6 per cent), Al_2O_3 (15·9 per cent), Fe_2O_3 (2·8 per cent), FeO (3·0 per cent), MgO (2·4 per cent), CaO (3·1 per cent), Na_2O (3·3 per cent), K_2O (2·9 per cent).

The analysis elements (as oxides or carbonates) were then incorporated into the matrix, to give a concentration of 1000 p.p.m. Other standards were prepared by diluting this one with matrix, the dilution factor being $\sqrt{0{\cdot}1}$. Thus the standards used contained 1000, 316, 31·6, 10 and 3 p.p.m. of the elements sought, respectively.

In order that the standards should burn smoothly in the d.c. arc they were first sintered for 24 hr at 1000°C. Further investigation showed that the matrix was eminently suitable.

Powdered graphite and an internal standard (tin oxide) were added (in the ratio graphite/tin oxide = 100/35) prior to arcing. Line intensities were measured using a densitometer and ratios of element line to internal standard line calculated. Working curves were drawn in which the intensity ratio of the analysis pair was

plotted on log–log paper against the concentration of the analysis element in each of certain standards. By reference to working curves, concentration of trace elements in the samples was determined.

Table 2. Analysis method

Spectrograph	A.R.L. 2 m grating type, with 24,000 lines/in., dispersion 5·2 Å/mm in first-order spectrum.
Excitation	250 V d.c., 13 A, 5 mm arc gap. Sample electrode the anode.
Slit	40 μ
Exposure	90 sec (light from the arc filtered to 3%).
Electrodes	Made from "Special" grade graphite rod.
Film	Eastman Kodak Spectrum Analysis Film 103–0.
Processing	3 min at 70°F in D-19 developer, 30 sec wash, 3 min in acid fixer, washed and dried.
Sample	60 mg sample of 1:1 mixture of rock powder and powdered graphite-tin oxide. Duplicate (or triplicate) analyses.

Table 3 lists the spectral lines used. The figures are taken from Ahrens (1950) and corrected to the first decimal place.

Reproducibility was calculated by methods advocated by Ahrens (1950, 1954) and is given in Table 4.

Table 3. Spectral lines

Ba	4554·0
Cr	4254·4
Mn	4034·5
Ni	3414·8
Cu	3274·0
V	3185·4
B	2494·7

Table 4. Reproducibility

	(%)
B	±13
Cr	±6
V	±7
Ni	±7
Cu	±6
Mn	±6
Ba	±6

Results and Geochemical Relations

Average trace element composition of the rocks

The means for each rock group analysed are recorded in Table 5. It is seen that certain differences exist between some of the rock groups but a grand average for all of the rocks has been calculated.

Statistically it was assumed that all the samples were drawn from populations which are normally distributed. Histograms were plotted for each element and in all cases except V and perhaps Ba there was a strong tendency toward unimodal character. This tendency in itself does not prove a normally distributed population, but makes it unlikely that the averages of numerous individual analyses depart appreciably from normality (see Figs. 1–7).

It may be pointed out that in calculating the final standard deviation for all of the rocks abnormally high and low values were in general included. This tends

Table 5. Average composition of Canadian Pre-Cambrian greywackes, argillites and low-grade schists

Rock groups	B	Cr	V	Ni	Cu	Mn	Ba
Arkosic and feldspathic greywackes	44	196	130	90	46	579	360
Volcanic greywackes	59	235	210	130	51	870	431
All greywackes	51	213	166	108	48	683	397
Argillites	86	200	181	106	42	580	470
Chlorite schists	53	257	248	172	72	570	372
Mica schists	52	222	148	88	62	642	472
All low-grade schists	52	231	177	112	65	636	444
Final average of (greywackes + argillites + low-grade schists)	67	212	175	108	47	626	441
Final standard deviation	50	77	78	58	30	280	206
Number of rocks	91	91	91	91	90	90	91

to raise the standard deviation, of course, but the author considered this to be the wisest course.

Comparison with other argillaceous rocks

When the values obtained for the Canadian Pre-Cambrian rocks are compared with the published data for marine argillaceous rocks it is found that, in general, the trace element content is closely the same. Hence a marine origin for the Canadian greywackes and argillites is strongly favoured.

The high values obtained for barium indicate that the rocks studied were not derived from predominantly basic terrains.

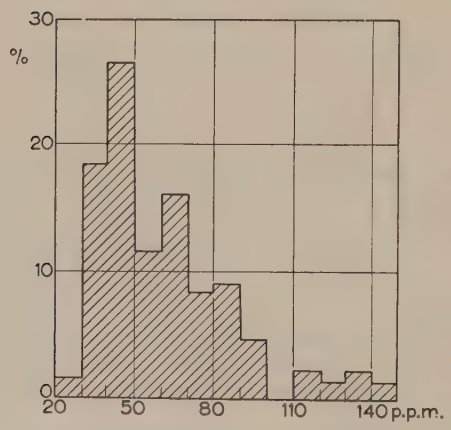

Fig. 1. Histogram for boron. Showing the range in the boron content of 89 greywackes, argillites, and low-grade schists.

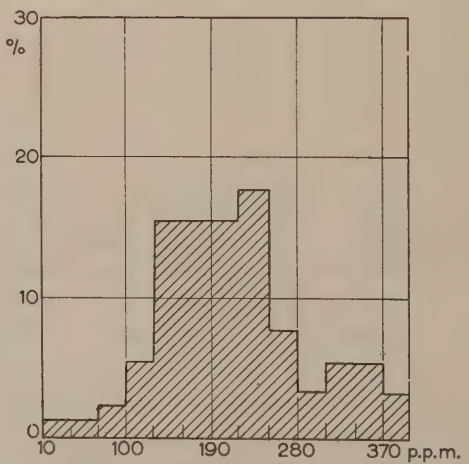

Fig. 2. Histogram for chromium. Showing the range in the chromium content of 90 greywackes, argillites, and low-grade schists.

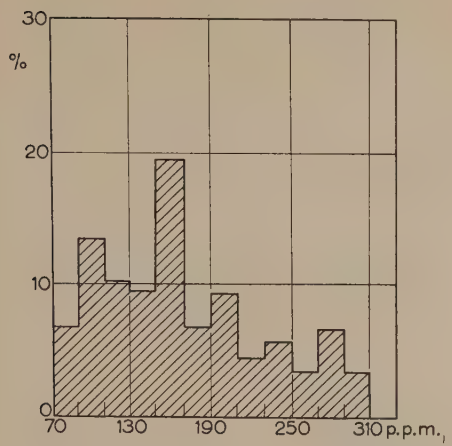

Fig. 3. Histogram for vanadium. Showing the range in the vanadium content of 87 greywackes, argillites, and low-grade schists.

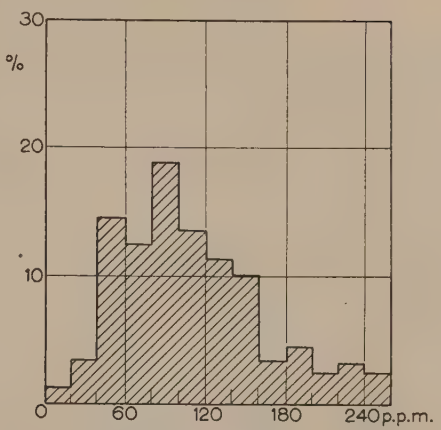

Fig. 4. Histogram of nickel. Showing the range in the nickel content of 90 greywackes, argillites, and low-grade schists.

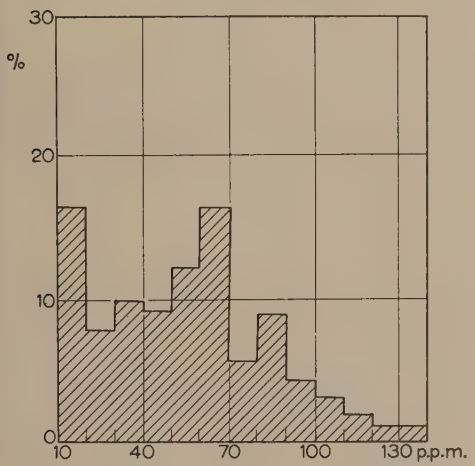

Fig. 5. Histogram for copper. Showing the range in the copper content of 90 greywackes, argillites, and low-grade schists.

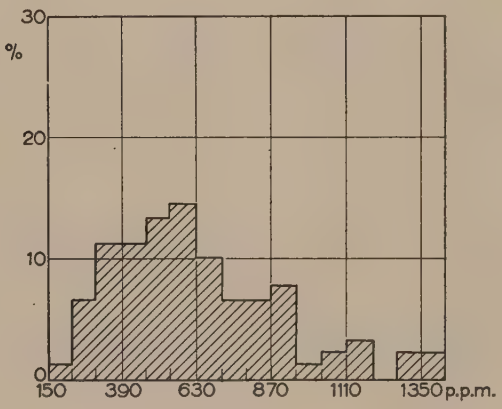

Fig. 6. Histogram for manganese. Showing the range in the manganese content of 90 greywackes, argillites, and low-grade schists.

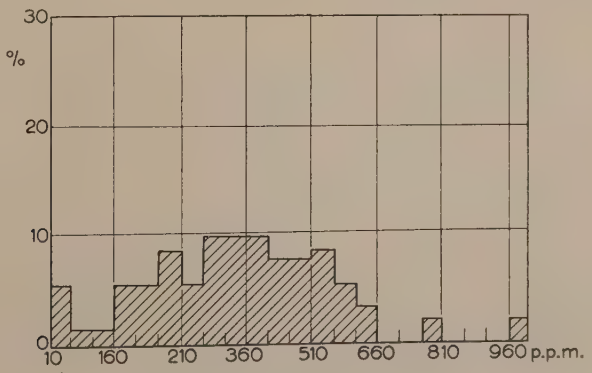

Fig. 7. Histogram for barium. Showing the range in the barium content of 91 greywackes, argillites and low-grade schists.

Range in composition

The range in composition is indicated by the standard deviations in Table 6.

Table 6. Averages and standard deviations for Canadian Pre-Cambrian greywackes, argillites and low-grade schists (p.p.m.)

Element	Average	s.d.	Ratio s.d. to average as %	Number of rocks
B	67	50	74	91
Cr	212	77	36	91
V	175	78	44	91
Ni	108	58	54	91
Cu	47	30	64	90
Mn	626	280	45	90
Ba	441	206	47	91

In this table the ranges are expressed as percentages of the mean; except for boron and perhaps copper, the relative ranges are about the same extending from about zero to twice the mean (see also Fig. 8). It follows that boron and copper

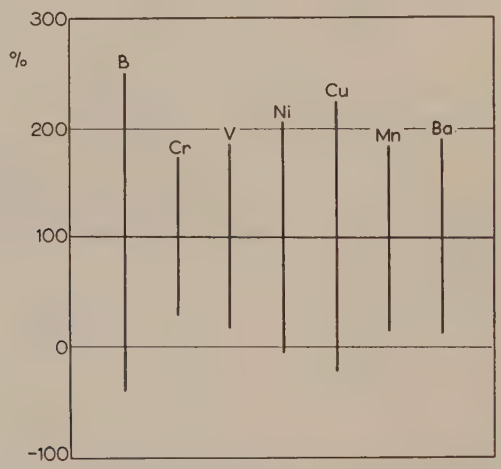

Fig. 8. Composition ranges for 95 per cent probability expressed as percentage of the mean.

are not regularly distributed in the sedimentary rocks. It is found that the ranges are of the same order of magnitude when plotted in p.p.m. on a logarithmic scale also. This is what would be expected on empirical grounds. Shaw (1954) in an excellent article has also considered this distribution law (namely that the range in composition extends from zero to about twice the mean value for almost every element) and concludes that "random fluctuations may then be expected, but with lower probability for high fluctuations from the average."

Enrichment and impoverishment

It is of interest to consider which elements have been concentrated and which diluted during the formation of argillaceous sediments compared with average crustal material.

In Column 2 of Table 7 are the abundance figures for argillaceous rocks obtained by the author and in Column 3 are the crustal abundances according to GOLDSCHMIDT. These crustal abundances cannot of course be taken as fact but should be of the right order of magnitude. SHAW (1954) suggests certain revisions in these crustal abundances (average igneous rock). He suggests, for example, 100 p.p.m. for Cr instead of 200 p.p.m. and 100 p.p.m. for V instead of 150 p.p.m.

Table 7. Crustal abundance of elements compared with their abundance in argillaceous sediments

Element	Abundance in Pre-Cambrian argillaceous sediments	Crustal abundance	Enrichment factor
B	67	3	22·3
Cr	212	200	1·1
V	175	150	1·2
Ni	108	80	1·3
Cu	47	70	0·7
Mn	626	1000	0·6
Ba	441	250	1·8

The last column in Table 7 gives the ratio of the figures in Columns 2 and 3 and indicates whether an element is concentrated or diluted in argillaceous rocks, as compared with the crust as a whole. Chromium and vanadium and nickel show little change while copper and manganese show some dilution. Barium clearly shows an enrichment, but it is boron that displays the most striking concentration. Boron is some twenty-two times more abundant in Pre-Cambrian argillaceous rocks than in the crust.

Relations between groups of elements

It might be expected that elements occurring in hydrolysate sediments would show interrelations with one another. Theoretically, similar behaviour between different elements with similar ionic potentials is to be expected. On examining his detailed analyses the writer noted that when the amount of chromium is high, so also is nickel, or that if chromium plus nickel is low, so also is vanadium (see Figs. 9 and 10). Further consideration, showed, however, that for other elements there is only a tendency for similar behaviour. Theoretically we should be able to express the relationships as a definite ratio but this does not appear to be the case.

Significance of the trace element content

The enrichment of boron in the rocks studied, compared with the crustal abundance generally accepted by geochemists has been shown to be considerable. Boron content of this order is generally taken to indicate a marine origin for

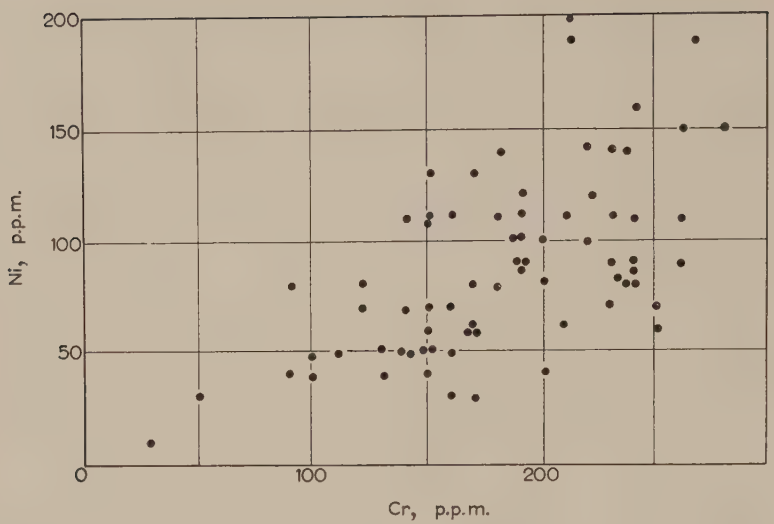

Fig. 9. Correlation of nickel and chromium in Canadian Pre-Cambrian argillaceous rocks.

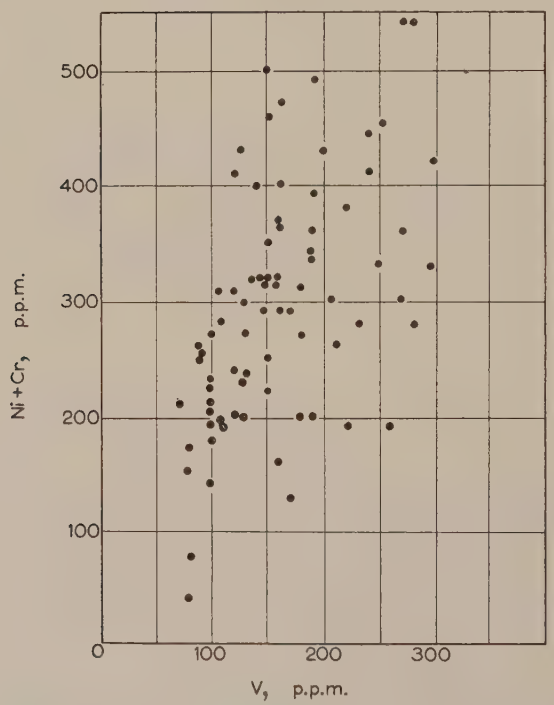

Fig. 10. Correlation of nickel plus chromium with vanadium in Canadian Pre-Cambrian argillaceous rocks.

sediments (LANDERGREN 1945). It should be pointed out that the boron content of greywackes and argillites from the cobalt series, generally considered to be glacial in origin, is only slightly less than the average for all greywackes (43 p.p.m. as against 51 p.p.m.) and about half that of all Pre-Cambrian argillites (86 p.p.m.) It is, of course, possible that the bedded cobalt sediments were deposited in marine or brackish waters near the ice front, and were not lacustrine. LANDERGREN (1945) has suggested that the boron content is a measure of the salinity of the water in which a sediment has been deposited. If we assume that this generalization holds also for even the oldest Pre-Cambrian rocks, then it appears that the seas at the time they were deposited did not differ markedly from those of the Paleozoic and later times in salinity. Further information is required regarding the minerals with which the boron is associated, before definite conclusions regarding its abundance in the original sediment can be made.

Chromium, nickel and vanadium in all Pre-Cambrian sediments studied differ but little from the crustal averages. They are considerably higher than the values given by SHAW (1954) for pelitic rocks, but correspond fairly well with the conclusions of other writers GOLDSCHMIDT (1954), CLARKE (1924). It is interesting to note that the volcanic greywackes are significantly higher than arkosic and feldspathic greywackes in these constituents (for chromium 235 p.p.m. compared with 196 p.p.m., for vanadium 210 p.p.m. as against 130 p.p.m. and for nickel 130 p.p.m. vs. 90 p.p.m.). The close similarity between the values obtained for normal greywackes, and for argillites and slates, in this and other studies, proves that greywackes do not result primarily from the accumulation of mechanically weathered fragments of basic rocks. The volcanic greywackes more closely approach this type, but still are probably diluted by normal argillaceous material.

Manganese and copper appear to have a rather erratic distribution in the rocks analysed. The averages agree fairly well with the values given by most other writers, except that SHAW gives much lower values for copper. There is nothing particularly notable about their occurrence, except that the manganese, like nickel and chromium, is higher in the volcanic greywackes than in the arkosic and feldspathic ones.

Barium also varies rather widely. The average barium content corresponds fairly well with earlier estimates (441 p.p.m. compared with 460 p.p.m. given by VON ENGLEHARDT (1936) for shales). The relatively high proportion of this element is not compatible with a dominantly basic source for the greywackes, and suggests that acid rocks made important contributions to the sediment from which these rocks were formed. The very low barium content of the cobalt (glacial) sediments is notable, as is the relatively high content of the volcanic greywackes (431 p.p.m.) compared with the arkosic and feldspathic types (360 p.p.m.).

Variation of the trace element content with time

One objective of the present investigation was to determine if there were any variations in trace element content with time. No significant variations in the amount of the trace elements could be established. Boron, it was thought, would be most useful in this connection, especially if the salinity of sea-water had varied significantly throughout the Pre-Cambrian. The results are tabulated in Table 8.

Table 8

Average boron content for all Pre-Cambrian rocks	(p.p.m.)	Average boron content for Pre-Cambrian argillites	(p.p.m.)
47 Proterozoic rocks	66	25 Proterozoic argillites	71
44 Archean rocks	68	19 Proterozoic argillites (excluding cobalt)	94
91 Pre-Cambrian rocks	67	16 Archean argillites	109

Slight differences appear in the averages for barium and for nickel plus vanadium plus chromium, as shown in Table 9.

The nickel, vanadium and chromium are somewhat higher in Archean rocks than in Proterozoic ones, and the reverse is true for barium. The differences are consistent with an increase of plutonic acid rocks compared with basic rocks as a

Table 9

Average content of Ni + V + Cr and Ba in Pre-Cambrian rocks

	Ni + V + Cr (p.p.m.)	Ba (p.p.m.)
47 Proterozoic rocks	443	448
44 Archean rocks	542	434
91 Pre-Cambrian rocks	495	441
25 Proterozoic argillites	435	490
16 Archean argillites	568	440

source for the sediments, an increase which one might expect from the known Pre-Cambrian succession in Ontario, but they are small compared with the standard deviation and only hint at this possibility.

Acknowledgements—This article is a summary of parts of the author's Ph.D. thesis entitled "A chemical and petrographic study of Pre-Cambrian sediments" completed in May 1955 at the University of Toronto.

The writer is indebted to Professor W. W. Moorhouse, who suggested the study, and to Professor F. G. Smith, both of the University of Toronto.

The writer is indebted to Mr. O. F. Carter and Dr. S. A. Ferguson for a number of specimens supplied for the investigation.

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Appendix

Sample localities

The sample localities and stratigraphic division from which the rock samples were collected are listed in Table 10. The publication numbers of government maps (e.g. O.D.M. 22h) are also given.

The last column of Table 10 lists the stratigraphic division to which the rocks have been allocated. Such information has been taken from the latest official government publications, such as reports and maps issued by the Ontario Department of Mines and the Geological Survey of Canada.

Table 10. Sample localities

No. and rock type	Locality and map No.	Stratigraphic division
Arkosic greywacke		
1	Northern outskirts Cobalt, N. Ontario. O.D.M. 22h	Cobalt
2	$1\frac{1}{4}$ miles N.E. Kearns, N. Ontario. O.D.M. 50a.	Cobalt
3	As above.	Cobalt
4	2 miles N.E. Virginiatown, N. Ontario. O.D.M. 50a.	Cobalt
5	Pallideau Island, Thessalon, Ontario.	Bruce
6	$\frac{3}{4}$ mile S. New Liskeard, N. Ontario. O.D.M. 22h.	Timiskaming
7	$1\frac{1}{2}$ miles S. New Liskeard, N. Ontario, O.D.M. 22h.	Timiskaming
8	2 miles S.W. Porcupine Lake, Timmins, N. Ontario, O.D.M. 47a.	Timiskaming
9	2 miles N.W. Porcupine Lake, Timmins, N. Ontario, O.D.M. 47a.	Timiskaming
10	As above.	Timiskaming
11	7 miles N.E. Beardmore, S.E. Lake Nipigon, Ontario. G.S.C. 308A.	Keewatin
Feldspathic greywacke		
12	N.E. shore Batchawana Bay, Lake Superior. O.D.M. 35b.	Keweenawan
13	Conglomerate Island, E. Thessalon, Ontario.	—
14	$1\frac{1}{2}$ miles S.W. of S. end Porcupine Lake, Ontario. O.D.M. 47a.	Timiskaming
15	7 miles N.E. Beardmore, W. Ontario. G.S.C. 308A.	Keewatin

Table 10 (*continued*)

No. and rock type	Locality and map No.	Stratigraphic division
Quartz greywacke		
16	N. Ramsay Lake, Sudbury, Ontario. O.D.M.22h.	Sudbury-Bruce
Volcanic greywacke		
17	Kaipokok River area, Labrador.	Proterozoic
18	Kaipokok River area, Labrador.	Proterozoic
19	Kaipokok River area, Labrador.	Proterozoic
20	Kaipokok River area, Labrador.	Proterozoic
21	$\frac{3}{4}$ mile S. New Liskeard, N. Ontario. O.D.M. 22h.	Timiskaming
22	As above.	Timiskaming
23	1 mile S. New Liskeard, N. Ontario. O.D.M. 22h.	Timiskaming
24	$1\frac{1}{2}$ miles S. New Liskeard, N. Ontario. O.D.M. 22h.	Timiskaming
25	E. Slimes Basin, Kirkland Lake, N. Ont. O.D.M. 1945–1.	Timiskaming
26	As above	Timiskaming
27	As above	Timiskaming
28	N.W. end Gull Lake, Kirkland Lake, Ont. O.D.M. 53a.	Timiskaming
29	As above.	Timiskaming
Argillites		
30	Hill of Keweenawan, Black Sturgeon River, Ont. G.S.C. 308A	Keweenawan
31	As above.	Keweenawan
32	Black Sturgeon River area, W. Ontario. G.S.C. 308A.	Keweenawan
33	Nonwatin Lake, S.W. Lake Nipigon, W. Ont. G.S.C. 308A.	Keweenawan
34	Batchawana Bay, Lake Superior, Ontario. O.D.M. 35b.	Keweenawan
35	N.E. shore Batchewana Bay, Lake Superior, Ont. O.D.M. 35b.	Keweenawan
36	As above.	Keweenawan
37	Near Chelmsford, Sudbury, Ontario. O.D.M. 22h.	Whitewater
38	Northern outskirts Cobalt, N. Ontario. O.D.M. 22h.	Cobalt
39	As above.	Cobalt
40	As above.	Cobalt
41	As above.	Cobalt
42	N.W. Hill Lake, S.W. Englehart, N. Ont. O.D.M. 50j.	Cobalt
43	As above.	Cobalt
44	Victoria Mine, S.W. Sudbury, Ontario. O.D.M. 22h.	Sudbury-Bruce
45	Ramsay Lake (Island), Sudbury, Ontario. O.D.M. 22h.	Sudbury-Bruce
46	Ramsay Lake, S.W. Sudbury, Ontario. O.D.M. 22h.	Sudbury-Bruce
47	Lake Panache, N. shore Lake Huron. G.S.C. 1971.	Bruce
48	Whiskey Lake, N. of Lake Huron, Ontario. O.D.M. 34c.	Bruce
49	N. W. end Whiskey Lake, Ontario. O.D.M. 34c.	Bruce
50	W. shore, Whiskey Lake, Ontario. O.D.M. 34c.	Bruce
51	Bear Lake, W. Whiskey Lake, Ontario. G.S.C. 1970.	Bruce
2	Algom Uranium Mine, Blind River, Ontario. G.S.C. 1970.	Bruce
53	As above.	Bruce
54	Pronto Uranium Mine, Blind River, Ontario. G.S.C. 1970.	Bruce
55	$3\frac{1}{2}$ miles W. Larder Lake, N. Ontario. O.D.M. 50b.	Timiskaming
56	4 miles W. Larder Lake, N. Ontario. O.D.M. 50b.	Timiskaming
57	As above.	Timiskaming
58	S.W. Crystal Lake, Lebel, N. Ontario. O.D.M. 53a.	Timiskaming
59	As above.	Timiskaming

Table 10 (*continued*)

No. and rock type	Locality and Map No.	Stratigraphic division
Argillites (contd).		
60	S.E. Mud Lake, Lebel, N. Ontario. O.D.M. 53a.	Timiskaming
61	Mattagami River, Ogden Township, Timmins, Ontario. O.D.M. 35g.	Timiskaming
62	S.W. of S. end Porcupine Lake, N. Ontario. O.D.M. 47a.	Timiskaming
63	1 mile S.W. Porcupine Lake, N. Ontario.	Timiskaming
64	As above.	Timiskaming
65	2 miles N.W. Porcupine Lake, Timmins, Ontario. O.D.M. 47a.	Timiskaming
66	As above.	Timiskaming
67	13 miles N.E. Beardmore, W. Ontario. G.S.C. 308A.	Keewatin
68	15 miles N.E. Beardmore, W. Ontario. G.S.C. 308A.	Keewatin
69	2 miles S. Beardmore, W. Ontario. G.S.C. 308A.	Keewatin
70	Rapids, Sturgeon River, 5 miles E. Lake Nipigon, Ont. G.S.C. 308A.	Keewatin
Chlorite schist		
71	$3\frac{1}{2}$ miles W. Larder Lake, N. Ontario. O.D.M. 50b.	Timiskaming
72	3 miles E. Larder Lake, N. Ontario. O.D.M. 50b.	Timiskaming
73	4 miles E. Cadillac, W. Quebec. G.S.C. 575A4.	Cadillac*
74	S.W. Tonawanda, S.E. Rouyn, W. Quebec. G.S.C. 399A.	Fournière*
75	4 miles E. Cadillac, W. Quebec. G.S.C. 575A.	Kewagama*
76	Steep Rock Lake, Rainy River, W. Ontario. O.D.M. 48b.	Seine*
77	Armot Island, nr. Fort Frances, W. Ontario. G.S.C. 98A.	Couchiching†
Mica schist		
78	Near Worthington Mine, Sudbury, Ontario.	Sudbury-Bruce
79	4 miles E. Cadillac, W. Quebec. G.S.C. 575A4.	Cadillac
80	As above.	Cadillac
81	River Héva, near N. Canadian Malartic, W. Quebec. G.S.C. 575A4.	Cadillac
82	As above.	Cadillac
83	Little Héva River, N. Canadian Malartic, W. Quebec. G.S.C. 575A4.	Cadillac
84	$1\frac{1}{2}$ miles N. Canadian Malartic, Western Quebec. G.S.C. 573A2.	Cadillac
85	S.W. Tonawanda, S.E. Rouyn, W. Quebec. G.S.C. 399A.	Fournière
86	4 miles E. Cadillac, W. Quebec. G.S.C. 575A.	Kewagama
87	As above.	Kewagama
88	4 miles E. Cadillac, W. Quebec. G.S.C. 575A.	Kewagama
89	As above.	Kewagama
90	Near Josephine Mine, Michipicoten area, Ontario. O.D.M. 1946–8.	Keewatin
91	Armot Island, near Fort Frances, W. Ontario. G.S.C. 98A.	Couchiching
92	Sapawe Lake, Rainy River, Ontario. O.D.M. 38e.	Couchiching

O. D. M. and G. S. C. are abbreviations for Ontario Department of Mines and Geological Survey of Canada.

* The terms Cadillac, Fournière, Kewagama and Seine are probably equivalent to the term Timiskaming.

† Couchiching is a term referring to rocks believed to be pre-Keewatin.

Statement of analysis

The analytical results (Tables 11 to 19) are expressed in parts per million (p.p.m.). Figures were obtained in all cases for the seven elements B, Cr, V, Ni, Cu, Mn and Ba. This group of elements (arranged in increasing ionic radius) constitutes each table. The rocks are grouped as follows: arkosic and feldspathic greywackes, volcanic greywackes, argillites and low-grade schists.

The mean concentration of each element of every group and sub-group have been calculated. Standard deviations have also been worked out for each group and also for all the rocks combined. In all calculations final results were obtained first before any rounding off of the figures took place.

Table 11. Arkosic and feldspathic greywackes

Sample No.	B	Cr	V	Ni	Cu	Mn	Ba
Arkosic greywacke							
1	40	200	210	100	20	260	30†
2	30	140	100	50	30	510	380
3	30	100	100	40	60	470	310
4	50	260	150	90	10	350	100
5	40	160	130	70	10	260	270
6	20	340	190	150	60	970	380
7	70	370	230	230‡	100	1300‡	630
8	40	170	100	60	50	420	270
9	60	230	160	140	60	580	480
10	40	180	130	90	40	790	350
11	60	140	110	50	60	750	410
Feldspathic greywacke							
12	30	160	70	50	40	300	610
13	40	150	100	60	30	700	360
14	60	180	90	80	60	410	180
15	60	190	110	110	60	650	580
16*	40	170	100	60	50	550	570

* Quartz greywacke, included with feldspathic greywacke for calculations.
† Glacial argillite, no mica in sample.
‡ Sample contains several grains of epidote—this may explain high figures.

Table 12. Average composition of 16 arkosic and feldspathic greywackes

	Samples 1–11		Samples 12–16		Samples 1–16	
	Mean	S.D.	Mean	S.D.	Mean	S.D.
B	44	17	46	—	44	14
Cr	208	95	170	—	196	72
V	147	53	94	—	130	43
Ni	97	64	72	—	90	45
Cu	46	30	48	—	46	23
Mn	606	350	522	—	579	278
Ba	328	183	460	—	360	145

Table 13. Volcanic greywackes

Sample No.	B	Cr	V	Ni	Cu	Mn	Ba
17	60	240	300	90	90	700	250
18	80	160	280	120	80	800	150
19	130	220	370	200	80	870	200
20	110	110	160	50	30	730	425
21	40	180	130	120	60	830	360
22	60	240	190	120	60	1130*	660
23	40	220	270	140	90	1300*	750
24	40	370	280	190	70	1170*	570
25	40	240	160	160	30	880	480
26	40	210	130	110	30	210†	650
27	50	350	160	120	30	1180	520
28	40	350	150	150	10	510	390
29	40	170	150	130	10	230	210

* Sample contains some hornblende and pyroxene minerals not found in the other volcanic greywackes.

† Figure unreliable, ignored for calculation.

Table 14. Average composition of volcanic greywackes

	Samples 17–29	
	Mean	S.D.
B	59	29
Cr	235	63
V	210	79
Ni	130	25
Cu	51	29
Mn	870	300
Ba	431	194

Table 15. Average composition of all types of greywackes

	Samples 1–29	
	Mean	S.D.
B	51	23
Cr	213	83
V	166	73
Ni	108	48
Cu	48	45
Mn	683	325
Ba	397	185

Table 16. Argillites

Sample No.	B	Cr	V	Ni	Cu	Mn	Ba
30	330	90	170	40	10	590	1020†
31	90	50	80	30	10	1400	750
32	110	120	260	70	20	490	660
33	70	30	80	10	30	670	350
34	40	220	360	100	30	900	540
35	70	210	250	120	10	1400	650
36	30	230	150	90	40	580	550
37	80	170	90	80	10	310	560
38	50	260	220	120	10	350	40‡
39	40	140	150	110	10	240	40‡
40	40	240	170	80	5	370	10‡
41	60	220	190	120	10	510	20‡
42	40	190	150	90	50	710	450
43	30	120	130	80	60	330	230
44	50	230	270	70	60	510	580
45	50	320	240	140	60	490	530
46	30	280	200	150	40	440	680
47	60	150	110	40	30	710	460
48	80	160	220	30	10	410	440
49	40	130	150	90	10	370	350
50	50	170	190	30	20	370	630
51	120	90	80	80	50	500	570
52	90	150	180	50	20	570	1010†
53	50	100	80	50	50	530	620
54	80	150	500	130	440*	490	530
55	50	210	240	230	50	440	210
56	60	440	200	250	110	590	200
57	80	210	190	180	80	720	200
58	30	230	160	140	20	670	390
59	80	350	270	190	90	430	670
60	60	250	160	40	40	830	700
61	140	180	140	140	50	330	290
62	390	340	310	80	80	290	880
63	430	300	150	160	60	680	410
64	90	320	80	250	50	390	260
65	60	190	120	220	100	510	470
66	30	140	100	70	10	550	320
67	50	230	190	110	80	880	620
68	60	190	170	100	70	940	450
69	60	150	100	120	70	670	490
70	70	240	180	80	80	650	450

* Figure unreliable and ignored for calculation.
† Rocks rich in potassic micas, which may explain high Ba content.
‡ Glacial argillites, potassic micas negligible, may explain low Ba. Figures included in calculations.

Table 17. Average composition of 41 argillites

	Samples 30–70	
	Mean	S.D.
B	86	87
Cr	200	81
V	181	82
Ni	106	59
Cu	42	28
Mn	580	252
Ba	470	227

Table 18. Low-grade schists

Sample No.	B	Cr	V	Ni	Cu	Mn	Ba
Chlorite schists							
71	70	260	250	190	140	830	280
72	80	330	270	360	10	720	260
73	30	150	90	110	50	320	200
74	60	330	410	210	120	1800*	260
75	30	240	160	80	90	1050	660
76	50	230	310	80	20	170	570
77	40	n.d.	5	n.d.	5	330	90†
Mica schists							
78	70	325	125	106	60	630	650
79	70	380	100	170	110	930	460
80	80	190	150	100	50	550	400
81	30	200	110	80	70	460	450
82	40	280	140	120	40	500	480
83	130	260	240	150	80	920	870
84	30	130	100	50	20	410	490
85	30	170	130	60	100	420	210
86	30	210	180	60	80	600	450
87	40	250	120	60	60	600	480
88	40	200	120	40	40	580	390
89	40	150	120	50	40	610	280
90	90	150	210	110	60	570	390
91	30	190	230	90	70	810	550
92	30	250	150	70	50	1050	540

* Rock contains fair amount of carbonate. Figure excluded from calculations.
† Potassic micas negligible in rock. Figure excluded from calculations.

Table 19. Average composition of 21 chlorite and mica schists

	Samples 71–77		Samples 78–92		Samples 71–92	
	Mean	S.D.	Mean	S.D.	Mean	S.D.
B	53	—	52	29	52	27
Cr	257	—	222	68	231	61
V	248	—	148	46	177	81
Ni	172	—	88	37	112	72
Cu	72	—	62	23	65	33
Mn	570	—	642	166	636	230
Ba	372	—	472	151	444	163

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Determination of thorium in the parts per million range in rocks*

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Abstract—A procedure is presented for the determination of thorium in the concentration range of 0·2 to 10 parts per million ThO_2 in felsic or mafic rocks. Thorium is extracted by mesityl oxide and purified by iodate precipitation from nitric acid medium containing tartaric acid and hydrogen peroxide. The thorium is determined spectrophotometrically with thoron from meso-tartaric acid medium.

Introduction

Studies on the geochemistry of thorium require data on the thorium content of various rocks. This paper presents a procedure that is useful for determination of thorium in the range of 0·2 to 10 p.p.m. thorium dioxide in felsic and mafic rocks. Above 10 p.p.m. thorium dioxide, advantage may be taken of the simpler procedure of Grimaldi, Jenkins and Fletcher (1957). Although main emphasis is placed on proving the validity of the proposed method, the data presented on the thorium contents of some rocks are of interest to geochemists.

Procedure and Discussion

The main steps in the procedure involve decomposition of a 5 g sample of rock, extraction of thorium nitrate with mesityl oxide, purification of thorium by iodate precipitation from nitric acid medium containing tartaric acid and hydrogen peroxide, and spectrophotometric determination of thorium with thoron in meso-tartaric acid medium.

The mesityl oxide extraction of thorium nitrate was originally introduced by Levine and Grimaldi (1950, 1954) for macro amounts of thorium, and has also been used by others (Banks and Byrd, 1953; Banks, Klingman and Byrd, 1953). Maréchal-Cornil and Picciotto (1953) have shown that thorium is quantitatively extracted in concentrations as low as 10^{-12} g of thorium/ml of solution. The iodate precipitation of thorium as described by Grimaldi, Jenkins and Fletcher (1957) is quantitative down to 1 μg of ThO_2 in 50 ml volume. The spectrophotometric determination of thorium with thoron in meso-tartaric acid medium allows the determination of as little as 1 μg of ThO_2 in a volume of 25 ml; details of this procedure are given by Fletcher, Grimaldi and Jenkins (1957). Only a few notes on the procedure are given here.

Samples are decomposed with a mixture of HF—HNO_3, followed by several evaporations with HNO_3 to decompose fluorides. Rocks containing appreciable amounts of magnesium give large precipitates of MgF_2 and it may be difficult to convert the insoluble fluorides to nitrates by nitric acid alone. In such cases, addition of no more than 1·5 g of boric acid in increments of about 0·5 g along

* Publication authorized by the Director, U.S. Geological Survey

with the nitric acid materially hastens the removal of fluoride. Ordinarily, complete decomposition of rocks is obtained by this treatment, and it is seldom necessary to collect undecomposed sample for solution by some other method such as a carbonate fusion and subsequent solution in nitric acid. Dunite may yield a residue of chromite which may be brought into solution after a sodium peroxide fusion.

Some mafic rocks contain appreciable amounts of titanium which may hydrolyse from solution on evaporation, especially with prolonged baking. Such a hydrolytic precipitate can be filtered, ignited and dissolved in HF. Any thorium in the hydrolytic precipitate is recovered from the HF solution as the insoluble ThF_4 by using a carrier such as yttrium or lanthanum, total carrier 15 mg, calculated as the oxide. If necessary, the carrier stock solution can be freed of thorium by careful addition of ammonium hydroxide (a small amount of H_2O_2 is helpful) until a small amount of precipitate of rare-earth hydroxide plus thorium is formed. The residue is filtered and rejected.

Thorium and rare-earth fluorides are filtered, ignited and dissolved in HNO_3, and the solution added to the reserved main solution. Finally, a solution containing 3·75 ml HNO_3 in a total volume of 25 ml is obtained.

After the addition and solution of 47·5 g $Al(NO_3)_3 \cdot 9H_2O$ crystals as a salting agent the solution is extracted twice with mesityl oxide, once with a 50 ml and then with a 25 ml portion. The aluminium nitrate is also effective in dissolving insoluble fluorides not decomposed by previous treatments.

After washing the organic layer with three separate 40 ml portions of aluminium nitrate wash solution (aluminium nitrate dissolved in (15 + 85) HNO_3 in the proportion of 9·5 g $Al(NO_3)_3 \cdot 9H_2O$ to 5 ml of the diluted HNO_3) the thorium nitrate is stripped from the organic solvent with two 45 ml portions of water.

The aqueous solution is evaporated and the organic matter destroyed with the aid of 10 ml HNO_3 and 2 ml $HClO_4$. The perchloric acid is then removed by heating on a sand bath at a temperature of 170° to 180°C. After adding 6 ml of 1 + 1 HNO_3 to dissolve the residue, the iodate separation and colorimetric estimation is made according to procedures described by Fletcher *et al.* (1957) and Grimaldi *et al.* (1957). Blanks should be carried through the analysis. The blank with ordinary reagent-grade chemicals is about 0·5 μg ThO_2.

Experimental Results

Table 1 illustrates the effectiveness of the fluoride separation of microgram amounts of thorium when 15 mg of either La_2O_3 or Y_2O_3 is used as a carrier. The iodate separation was used to free thorium from the carrier and the determination of thorium was made spectrophotometrically with thoron. Thus the recoveries include any errors introduced by the iodate separation and colorimetric estimation.

Experiments on a 5 g sample of San Marcos gabbro from the southern California batholith spiked with known amounts of thorium and carried through the complete procedure gave excellent recoveries of the thorium added, as shown in Table 2.

The reproducibility of the results on a standard diabase W-1 and granite G-1 (Fairbairn *et al.*, 1951; Schlecht, 1951) are shown in Table 3. The first four represent separate determinations on each sample, but run at the same time. The

Table 1. Effectiveness of lanthanum or yttrium fluoride as a carrier for thorium fluoride (15 mg of each carrier used, calculated as oxide)

Carrier	Thorium added (μg ThO_2)	Thorium found (μg ThO_2)	Percentage recovered
Yttrium	3·02	2·9	97
Yttrium	3·02	3·2	107
Yttrium	15·09	14·7	97
Yttrium	15·09	15·7	104
Yttrium	30·18	29·8	99
Yttrium	503	500	99
Lanthanum	30·18	30·5	101
Lanthanum	503	490	97

Table 2. Recoveries of thorium added to gabbro

ThO_2 added (p.p.m.)	ThO_2 found* (p.p.m.)
0·4	0·4
0·6	0·6
1·0	1·0
2·0	2·0
5·0	4·5
6·0	5·8
10·0	9·8

* Thorium content of the gabbro, 0·3 p.p.m. ThO_2, was subtracted.

Table 3. Reproducibility of results on standard diabase W–1 and granite G–1

ThO_2 (p.p.m.)	
Diabase W-1	Granite G-1
2·1*	52*
2·1*	52*
2·1*	52*
2·1*	52*
2·2†	51†
2·3†	51†
3·6‡	61‡

* Run simultaneously.
† Re-run one month later.
‡ By γ-ray spectrometry. P. M. Hurley, Massachusetts Institute of Technology (personal communication).

excellent reproducibility for these is clearly fortuitous. The next two determinations on each sample were made a month later. Also shown are the results obtained by P. M. Hurley, Massachusetts Institute of Technology (personal communication), by γ-ray spectrometry. Hurley states that the thorium content of W-1 was too low for a good γ-ray determination. In the range below 1 p.p.m. a greater scatter

Table 4. Comparison of spectrophotometric and mass spectrometric results on two basalts

Sample	Spectrophotometric		Mass spectrometric* ThO_2 (p.p.m.)
	Weight of sample (g)	ThO_2 (p.p.m.)	
Basalt of the Hualalai volcanic series, Hawaii Island, T. H. (western branch of 1800 flow)	3·00	3·9	1·8
	0·80	4·2	
Snake River basalt (1·8 miles north of Shoshone, Idaho on U.S. Highway 93)	5·00	2·9	2·3
	1·00	3·2	

* Analyst, George Tilton, Geophysical Laboratory, Carnegie Institution of Washington (personal communication).

in results was obtained. For example, the results of three determinations made on different dates on the San Marcos gabbro were 0·3, 0·4, and 0·2 p.p.m. ThO_2. Here variations in blank values exert a significant effect.

Table 5. Thorium determinations on Laramide intrusive rocks from the Front Range, Colorado

Sample no.	Description	ThO_2 (p.p.m.)	
		Without mesityl oxide extraction*	With mesityl oxide extraction†
P 118L	Alkalic rhyolite	100, 107	105
P 370L	Rhyolite	33, 36	33
P 581L	Alkalic rhyolite	213, 218	240
P 633L	Alkalic rhyolite	75, 84	74
P 914L	Syenodiorite	39, 37	27
P 640L	Granodiorite	17, 17	17

* Analyst, Marjorie Malloy, U.S. Geological Survey, method of Fletcher *et. al.* (1957) and Grimaldi *et al.* (1957).

† Method described in this report.

The results on two basalts obtained from George Tilton, Geophysical Laboratory, Carnegie Institution of Washington, and previously analysed by Tilton by an isotope dilution mass-spectrometric procedure, are compared in Table 4.

The reason for the discrepancies between the two methods is not definitely known. TILTON states that only single determinations were made and that the basalt of the Hualalai volcanic series was not completely decomposed in his procedure, much of the spinel being unattacked and discarded.

Table 5 gives a comparison of thorium determinations by two methods on Laramide intrusive rocks from the Front Range, Colorado. In the first method, a 0·3 g sample is used and the mesityl oxide separation is omitted. The second set was analysed by the procedure of this report on 5 g samples.

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Argonbestimmungen an Kaliummineralien—V

Altersbestimmungen nach der Kalium-Argon-Methode an Mineralien und Gesteinen des Schwarzwaldes

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Abstract—This paper deals with systematic analyses of the foundation of the Black Forest according to the potassium—argon method. As this region has been well mapped, and as the sequence of ages of the petrogenetic main phases is known, there is a possibility of co-ordinating, in this region, the potassium–argon method with the mineralogical and geological examinations and to test at the same time the efficiency of the potassium–argon method.

The measurements showed that an exact correspondence to the relative time scale could be attained and that the determination of age according to the potassium–argon method can be used to examine special problems of the petrogenetic evolution.

1. Allgemeines zur Kalium–Argon-Methode

Nach den eingehenden Untersuchungen über die Anwendbarkeit der Kalium–Argon-Methode, die wir in der letzten Mitteilung beschrieben, sollen hier nochmals die Vorteile dieser Methode kurz zusammengefasst werden:

(a) *Die Edelgasanalyse.* Von allen Methoden, die bis heute zu Altersbestimmungen von Gesteinen und Mineralien entwickelt wurden, sind die K/A- und die U/He-Methoden dadurch ausgezeichnet, dass die Tochtersubstanzen der radioaktiven Elemente Edelgase sind. Eine Bestimmung des Edelgasgehaltes von Mineralien ist aber bedeutend einfacher und vor allem viel schneller durchzuführen als die ungenaueren analytischen Trennungsverfahren, die bei den anderen Methoden der Altersbestimmung ausgeführt werden müssen. Ferner bietet die K/A-Methode gegenüber der U/He-Methode den Vorteil, dass die Diffusionskonstante von Argon in allen Mineralien kleiner ist als die von Helium und deshalb der U/He-Methode vorzuziehen ist.

(b) *Die allgemeine weite Verbreitung der Kaliummineralien.* Bei der K/A-Methode macht es keine Schwierigkeiten, Material zu finden, an dem die Altersbestimmung ausgeführt werden kann, da von allen vorkommenden Mineralien der Feldspat mit 59% das weitaus häufigste Mineral der zugänglichen Erdkruste ist. Allein 17% sind reiner Kalifeldspat, sodass die Möglichkeit gegeben ist, absolute Altersbestimmungen an einem sehr grossen und geologisch differenzierten Gesteinsmaterial durchzuführen. Es sind daher auch systematische Altersuntersuchungen im älteren Grundgebirge der Erde möglich, wo andere absolute geologische Datierungsmöglichkeiten nicht mehr zur Verfügung stehen.

(c) *Spezielle Probleme der petrogenetischen Entwicklung.* Für die Anwendung der radioaktiven Altersbestimmung sind durch die K/A-Methode neue Wege geöffnet, da mit dieser Methode sehr spezielle Probleme der petrogenetischen Entwicklungsphasen untersucht werden können (wie z.B. Altersfolgen magmatischer Gesteine

eines Orogens oder Altersunterschiede innerhalb eines Intrusivkörpers). Weiterhin besteht z.B. die Möglichkeit, anatektische Umwandlungen von Gesteinskomplexen (verschiedene Stadien der Wiederaufschmelzung von Gesteinen) altersmässig zu erfassen, da bei jeder teilweisen Mobilisierung die Tochtersubstanz Argon aus der Schmelze entweicht. Diejenigen Methoden der Altersbestimmung, bei denen das inaktive Tochterelement ein nichtgasförmiges Element ist, erfassen im allgemeinen nur den Zeitpunkt der ersten Auskristallisation, nicht aber Zeitabschnitte, wo eine teilweise Mobilisierung des Materials erfolgte.

In dieser Arbeit werden systematische Untersuchungen über das Grundgebirge des mittleren und südlichen Schwarzwaldes mitgeteilt, da dieses Gebiet sehr gut kartiert und die *relative Altersfolge* der petrogenetischen Hauptphase durch Arbeiten von K. R. Mehnert und D. Hoenes bekannt ist. Es bietet sich hier daher die Möglichkeit, die Kalium–Argon-Methode mit den mineralogischen und geologischen Untersuchungen in diesem Gebiet zu koordinieren und die Leistungsfähigkeit der Kalium–Argon-Methode zu überprüfen. Die Altersbestimmung der einzelnen Entwicklungsphasen dieses Gebietes soll ferner absolute Zeitmarken und ausserdem eine genaue zeitliche Zuordnung für einige Entstehungsvorgänge geben, die auf Grund der petrographischen Analyse nicht eindeutig in das magmatische Entwicklungsschema eingeordnet werden können.

2. Messtechnik

Die für die folgenden Messungen verwendete Aufschluss- und Messtechnik haben wir bereits in früheren Arbeiten beschrieben. Es sei jedoch hier noch darauf hingewiesen, dass erst durch die Verwendung eines Hochfrequenzschmelzofens Argonmessungen und Altersbestimmungen an sehr inhomogenen Materialien ausgeführt werden konnten, bei denen der Kaligehalt innerhalb sehr kleiner Bereiche Schwankungen bis zu 30% aufweist, da wir jetzt die Kaliumanalyse direkt am Schmelzgut ausführen. Bei dieser Aufschlusstechnik waren wir nicht mehr darauf angewiesen, die Kaliumanalyse an einem benachbarten Stück der zur Argonmessung verwendeten Probe auszuführen. Damit war aber eine beträchtliche Fehlerquelle der Altersbestimmung eliminiert, und wir konnten deshalb die inhomogenen Materialien wie Granite, Grauwacken, Ortho- und Paragneise, Porphyre, Syenite und andere Gesteinskomplexe zur Altersbestimmung heranziehen. Durch mehrere Testversuche konnte gezeigt werden, dass selbst bei Temperaturen von 2000°C im HF Ofen innerhalb der Fehlergrenze der K-Bestimmung von +1% kein Kalium-Verlust aus den SiO_2-reichen Schmelzen nachzuweisen war. Die untersuchten Proben wurden in dankenswerter Weise von J. Zähringer massenspektrometrisch auf Luftargon untersucht und korrigier (Smits und Zähringer, 1955).

3. Ergebnisse

Die Auswahl der zur Altersbestimmung verwendeten Gesteinsproben wurden nach den Gesichtspunkten getroffen, die wir in unserer letzten Mitteilung IV besprochen haben.

In der folgenden Tabelle 1 sind alle Einzelmessungen an den Materialien aufgeführt und in Tabelle 2 sind die Maximalwerte für die einzelnen Gesteine und Mineralien übersichtlich dargestellt. Zur Berechnung der Alterswerte wurden folgende Zerfallskonstanten verwendet:

$$\lambda_\beta = 4{,}77 \times 10^{-10}\text{a}^{-1} \qquad H_\beta = 1{,}45 \times 10^{9}\text{a}$$
$$\lambda_K = 5{,}68 \times 10^{-11}\text{a}^{-1} \qquad H_K = 1{,}22 \times 10^{10}\text{a}$$
$$\lambda_{\text{total}} = 5{,}34 \times 10^{-10}\text{a}^{-1} \qquad H = 1{,}30 \times 10^{9}\text{a}$$
$$\lambda_K : \lambda_\beta = 0{,}120$$

Wie aus Tabelle 1 zu ersehen ist, schwanken die Einzelmessungen aller Materialien bis auf die Grauwacken–Paragneise um maximal 4–5%, obwohl sich teilweise der Kaliumgehalt an demselben Material von Probe zu Probe um 30% ändert. Die grossen Abweichungen der Einzelmessungen an den Grauwacken–Paragneisen sind nicht ohne weiteres zu verstehen. Eine Deutung für die unterschiedlichen Messergebnisse bei diesen Materialien wird von K. R. Mehnert in No. 6 unter "Argonbestimmungen an Kaliummineralien" gegeben.

In der Tabelle 2 sind die maximalen Alterswerte von den einzelnen Gesteinsproben zusammengestellt, da bei allen untersuchten Mineralien mit geringen Argonverlusten zu rechnen ist, und deshalb die maximalen Alterswerte dem wirklichen Alter der Gesteine und Mineralien am nächsten kommen.

4. Diskussion

Es sei hier nur hervorgehoben, dass die absolute Altersbestimmung nach der Kalium–Argon-Methode die richtige Reihenfolge der verschiedenen petrogenetischen Entwicklungsphasen erfasst und in guter Übereinstimmung mit der aus den petrographischen Analysen bekannten relativen Zeitskala steht. Eine genauere Diskussion der einzelnen Materialien und der geologischen und mineralogischen Zusammenhänge wird von K. R. Mehnert in No. 6 in "Argonbestimmungen an Kalium" gegeben.

Bei der Diskussion der Messergebnisse darf trotz der guten Übereinstimmung der einzelnen Messungen an einem Material nicht ausser Acht gelassen werden, dass auch eine Altersbestimmung nach der Kalium–Argon-Methode immer mit mehr oder weniger grossen Fehlern behaftet ist. Zur besseren Übersicht wollen wir alle möglichen Fehlerquellen nochmals zusammenstellen:

(I) *Systematische Fehler*

(a) *Verzweigungsverhältnis des* ^{40}K. Während die Zerfallskonstante λ des ^{40}K auf 3–4% genau bekannt ist, liegt der Fehler für das Verzweigungsverhältnis $\lambda_K : \lambda_\beta = 0{,}120$ etwa bei 10%. Da dieses Verzweigungsverhältnis direkt in die Alterswerte eingeht, kann sich die Zeitskala in diesen Grenzen verschieben, nicht aber die relativen Zeitabstände der untersuchten Proben, worauf in dieser Arbeit das Hauptgewicht gelegt wurde.

(b) *Argonverluste der Mineralien.* Der Argonverlust der Mineralien ergibt einen systematischen Fehler nach jüngeren Alterswerten, der je nach der Qualität des Materials sehr grosse Ausmasse annehmen kann. (Siehe Mitteilung IV).

Tabelle 1. Ergebnisse der Einzelmessungen

Material	Lfd. Nr.	% Kal.	mm^3 rad. ^{40}A / g. Material	m^3 rad. ^{40}A / g. Material	Alter in 10^6a
Orthoklas	403	11	0,115	1,05	253
Waldkirch	406	10,89	0,114	1,05	253
Pegmatit	407	10,14	0,101	0,996	240,5
	421	10,62	0,110	1,035	250
	422	10,90	0,112	1,03	249
Biotit					
Stbrch.	66	6,51	0,069	1,06	255
Hechtsberg	67	5,59	0,059	1,058	254
Feldspat	68	6,57	0,0662	1,005	243
Hechtsberg	69	5,32	0,052	0,98	237
Pegmatit	70	1,16	0,0119	1,03	248,5
Mischgneis					
Metablastit	225	2,43	0,02665	1,09	262
Artenberg NW	224	2,33	0,0249	1,07	258
Granitporphyr					
Geisbaumhalde	23	4,15	0,0456	1,10	264
Nö. Caritas	214	4,22	0,046	1,10	264
Bl. Feldberg	204	4,30	0,0497	1,155	276
Kfs. aus Granitporphyr	2	9,96	0,107	1,075	260
Geisbaumhalde	15	10,25	0,111	1,08	260,5
Bl. Feldberg	17	10,27	0,105	1,02	246
	516	10,89	0,119	1,09	262
Wehra-Wiesental					
Granit	20	2,44	0,0238	0,976	236,5
(Ohne Grossfeld-	21	2,07	0,0203	0,981	237,5
spatkristalle)	60 Str. Bl.	1,75	0,0172	0,980	237
Kfs.-Grosskristalle	205	9,64	0,1085	1,128	270
Wehra-Wiesental-	212	9,48	0,1082	1,14	273
Granodiorite	63	9,58(M)	0,11	1,15	275,5
Holzschlag					
Albtalgranit	4	6,85	0,0783	1,142	273,5
Tiefenstein	9	6,70	0,0718	1,072	258
	220	7,89	0,0903	1,15	275,5
Kfs. Grosskristalle aus	1	9,55	0,116	1,218	290
Albtalgranit	13	10,23	0,123	1,202	287
	14	9,84	0,119	1,212	289,5
	506	10,40	0,121	1,165	280

Tabelle 1—*fortsetzung*

Material	Lfd. Nr.	% Kal.	mm^3 rad. ^{40}A / g. Material	mm^3 rad. ^{40}A / g. Material	Alter in 10^6a
Kfs. Metablastengestein	201	4,47	0,057	1,272	302,5
Utzenfeld	213	4,37	0,0354	1,22	291
	5	4,58	0,061	1,33	314
Kfs. Megablasten	202	5,75	0,0655	1,14	273
aus Metablastit	208	5,91	0,071	1,20	288
	211	6,01	0,070	1,17	280
Kinzigit	54	2,27	0,0263	1,16	278
Schenkenzell	55	2,44	0,029	1,19	284,5
	227	2,25	0,027	1,20	286
H. Paragneis	203	2,21	0,0288	1,30	308
	207	2,17	0,0278	1,28	303,5
	219	2,03	0,0256	1,26	300
Syenit Vortal	228	2,92	0,0376	1,29	306
	229	2,91	0,0376	1,293	306,5
Orthogneis	521	1,87	0,023	1,23	291
reliktisch	222	1.74	0,0245	1,41	332
Einetwald	223	1,94	0,0254	1,30	308
Grauwacken	217	3,13	0,0402	1,265	302
Paragneis	49	3,32	0,0451	1,358	321
Steinbruch	52	3,18	0,0372	1,17	280
Oberwinden	53	3,36	0,0385	1,15	275,5
	62	3,02	0,026	0,86	210
Paragneis	209	2,47	0,0366	1,48	347,5
Metatexit	221	2,14	0,0304	1,42	335
Steinbruch	33	2,36	0,0353	1,50	351
Grauwacken	47	2,06	0,0318	1,545	362
Paragneis	48	2,28	0,0276	1,21	289
Frohnbach	50	2,25	0,0187	0,832	203
	51	2,21	0,022	0,995	240
	216	2,08	0,0226	1,09	262
	61 Str. Bl.	2,20	0,016	0,728	179

Tabelle 2. Maximalwerte der Einzelmessungen

Fundort	Material	Alter in 10^6a
(1) Waldkirch	Orthoklas	253 ± 10
(2) Hechtsberg	Anorthoklas	248,5 ± 10
	Biotit	255 ± 10
(3) Artenberg NW	Mischgneis-Metablastit	262 ± 10
(4) Geisbaumhalde	Granitporphyr	276 ± 10
	Kfs. aus Granitporphyr	262 ± 10
(5) Wehra-Wiesental	Kfs.-Grosskristalle	275 ± 10
Holzschlag	Granit	237 ± 10
(6) Tiefenstein	Albtalgranit	275 ± 10
	Kfs-Grosskristalle aus Albtalgranit	290 ± 10
(7) Utzenfeld	Kfs-Megablasten aus Metablastit	288 ± 10
	Kfs-Metablastengestein	314 ± 10
(8) Schenkenzell	Kinzigit	286 ± 10
(9) Holzschlägermatte	Paragneis Diatexit	308 ± 10
(10) Vortal	Syenit	306 ± 10
(11) Einetwald	Orthogneis	332 ± 10
(12) Oberwinden	Grauwacken Paragneis	321
(13) Oberwinden	Paragneis Metatexit	351 ± 10
(14) Frohnbach	Grauwachen	362

Dieser Fehler lässt sich nur durch sorgfältige mikroskopische Auswahl des Materials vermeiden und dadurch auf einen Wert von ungefähr 5% herabdrücken.

(II) *Zufällige Fehler*

(a) *Die Mengenbestimmung des Argons* einer Probe lässt sich auch mit einem guten McLeod mit einem Fehler von 2% ausführen.

(b) *Die massenspektrometrische Kontrolle* des Luftargongehaltes einer radiogenen Probe ist ebenfalls mit einem Fehler von 1–2% behaftet.

(c) *Die Kaliumanalyse* des untersuchten Materials ist mit einer Genauigkeit von 1 bis 2% möglich.

Die Einzelmessungen dürften damit in einer relativen Zeitskala nur um maximal 10% schwanken, was auch experimentell beobachtet wurde. Fast durchweg zeigen aber die Einzelmessungen von einem Mineral nur eine Abweichung von 5%. Die absoluten Alterswerte können dagegen mit einem Fehler behaftet sein, der aber sicher nicht über 15 bis 20% liegt.

Die Kaliumanalysen der untersuchten Proben wurden flammenphotometrisch im Mineralogischen Institut von A. Willgallis ausgeführt. In den mineralogischen Fragen haben uns Prof. Dr. K. R. Mehnert, Dr. G. Rein und Dr. R. Metz beraten. Die Deutsche Forschungsgemeinschaft unterstützte die vorgenommenen Untersuchungen mit einer Sachbeihilfe.

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Argonbestimmungen an Kaliummineralien—VI

Die geologische Entwicklung des Schwarzwald-Grundgebirges anhand absoluter Altersbestimmungen nach der K-A-Methode

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Abstract—The age of 14 samples of variscian and prevariscian rocks of the Black Forest (Southern Germany) has been measured by means of the K–A-method. The samples were taken in order of their petrogenetic sequence, which was known from previous petrographic work. The accuracy and precision of the method has been discussed for some granites, pegmatites and porphyries of known age (lower/upper Carboniferous).The determined age of the metamorphic and granitized rocks depends on the time of the first formation of the original rock (i.e. sedimentary educt of paragneisses) but is strongly influenced by the age and intensity of the regional granitization (loss of A). This age has been determined as early-variscian. The age of the sedimentary educt is probably Pre-cambrian.

In der vorliegenden Untersuchung, die in Zusammenarbeit mit W. Gentner und W. Kley (s. Teil V dieser Veröffentlichungen) entstanden ist, wurde an 14 Proben das *absolute Alter einer Gesteinsreihe* ermittelt, die repräsentativ ist für die ältere geologische Geschichte des Schwarzwaldes.

Eine solche *Reihenuntersuchung* ist möglich durch Anwendung der K-A-Methode. Die Altersbestimmungen nach dem U-und Th-Verfahren beziehen sich dagegen i.a. auf *Einzelanalysen*. Minerale, die U oder Th in genügender Konzentration enthalten, sind entweder extensiv weit verbreitet aber nur von geringer Intensität der Vorkommen (z.B. Th-haltiger Zirkon ist in Graniten etwa in der Grössenordnung von 0,05% vorhanden), oder die Intensität der Vorkommen ist gross, ihre Extensität jedoch klein (Uran-Lagerstätten). Es kommt hinzu, dass letztere genetisch an wenige, ganz bestimmte Phasen der Lagerstättenbildung geknüpft sind (Hydrothermale Co-Ni-Ag-Bi-U-Formation, sedimentäre aride U-Konzentrationslagerstätten, bituminöse Schiefer). Altersbestimmungen an diesen Gesteinen sind daher nur für bestimmte geologische Fragestellungen brauchbar. Für grössere Zusammenhänge ist es jedoch erwünscht, Gesteinsreihen, die nach genetischen und petrographischen Gesichtspunkten entnommen sind, möglichst ohne weitere Aufbereitung auf ihr absolutes Alter untersuchen zu können. Die gleichzeitig grosse Intensität und Extensität der K-haltigen Minerale erlaubt solche Untersuchungen nach der K-A-Methode.

Wie Gentner und Kley beschrieben haben, ist bei dieser Methode eine *Abtrennung* der untersuchten K-Minerale nicht mehr nötig. Dadurch erleichtern sich viele geologisch-petrographische Probleme der Probenauswahl. So können

auch relativ kleinkörnige und "verwachsene" Gesteine analysiert werden, da eine Pulverisierung und Trennung der Minerale entfällt. Zugleich wird damit die Gefahr eines A-Verlustes vor der Schmelzung ausgeschaltet.

Schliesslich wird der K-Wert am Schmelzkuchen selbst bestimmt, dadurch entfällt die Frage, ob A- und K-Analyse an völlig gleichem Material vorgenommen wurden. *Das Problem der Homogenität des Ausgangsmaterials* spielt daher keine Rolle. Es können auch Sedimente, Gneise und anatektische Gesteine grösster Heterogenität untersucht werden, was im vorliegenden Falle für die Granitisierungsgesteine des Schwarzwaldes weitgehend ausgenutzt worden ist.

Die *Reihenfolge* der untersuchten Proben ist folgendermassen: Sie geht aus von altersmässig bekanntem Material. Hieran wurde die Methode apparativ entwickelt und ihre Fehlergrenze bestimmt. Als die grundsätzliche Brauchbarkeit der Methode feststand, wurde altersmässig unsicheres und schliesslich völlig unbekanntes Material analysiert. In dieser Reihenfolge werden auch die Proben im folgenden besprochen:

Untersuchungsergebnisse

1. *Kalifeldspat Waldkirch*

Das Material entstammt einem Pegmatitgang aus mobilisiertem Hornblendegneis (Fdpkt: Stbr. am Güterbahnhof Waldkirch). Der Kalifeldspat ist relativ rein und in grossen Kristallen gewinnbar. An diesem Material wurden die ersten Versuche durchgeführt, um die Methode auf ihre Genauigkeit zu prüfen.

Die Versuche wurden bereits als vorläufige Mitteilung veröffentlicht: W. Gentner, F. Jensen und K. R. Mehnert: "Zur geologischen Altersbestimmung von Kalifeldspat nach der Kalium-Argon-Methode" (Ztschr. f. Naturf. 9*a*, 1954, S. 176). Es ergab sich ein Alter von 223.10^6 a. Da dem Pegmatit aus geologischen Gründen ein Alter zwischen Oberkulm und Oberkarbon zuzusprechen ist, lag dieser Wert nach der Zeitskala A von Holmes (1947), die für die genannte Zeit ein absolutes Alter von etwa $260–220.10^6$ a angibt, bereits recht gut. Schmelzungen mit dem Hochfrequenzofen ergaben etwas höhere Werte:

Material	Lfd. Nr.	% K	$\frac{mm^3 \text{ rad. } A^{40}}{g. \text{ Material}}$	$\frac{mm^3 \text{ rad. } A^{40}}{gr. \text{ K}}$	Alter (10^6 a)
Orthoklas aus Pegmatit (Waldkirch)	403	11,0	0,115	1,05	*253*
	406	10,89	0,114	1,05	253
	421	10,62	0,110	1,035	250
	422	10,90	0,112	1,03	249
	407	10,14	0,101	0,996	240,5
				Mittelwert:	249 ± 10
				Maximalwert:	253 ± 10

2. *Kalifeldspat und Biotit aus Pegmatit vom Hechtsberg*

Bei diesem Versuch wurden grosse Kalifeldspat- und Biotit-Kristalle aus dem

grobkörnigen Pegmatit ausgelesen und getrennt dem gleichen Verfahren unterworfen. (Fdpkt. : Stbr. Hechtsberg b. Hausach).

Die Versuchsdaten waren:

Material	Lfd. Nr	% K	$\frac{mm^3 \text{ rad. } A.^{40}}{g \text{ Material}}$	$\frac{mm^3 \text{ rad. } A^{40}}{gr. K}$	Alter (10^6a)
Biotit	66	6,51	0,069	1,06	255
(Hechtsberg)	67	5,59	0,059	1,059	254
Kalifeldspat	70	1,16	0.0119	1,03	*248,5*
(Hechtsberg)	68	6,57	0,0662	1,005	243
	69	5,32	0,052	0,98	237

Da die Fehlergrenze (auf Grund der bei anderen Versuchen ermittelten Streuung) etwa mit $\pm 10^6$ a anzugeben ist, liegen die Einzelwerte innerhalb bzw. in der Nähe dieser Fehlergrenze. Die etwas höheren Werte für Glimmer dürften aber reell sein, da Versuche von Gentner und Kley an norwegischen Gesteinen zu den gleichen Abweichungen geführt haben, und andere Arbeiten (Folinsbee u.a. 1956; Wetherill u.a. 1956; Amichranow u.a. 1955) das Gleiche berichten. Ob dieser "Altersunterschied" tatsächlich auf einem höheren Alter der Pegmatit-Glimmer beruht oder auf der geringeren Möglichkeit eines Argonverlustes aus dem Glimmergitter, kann vorläufig nicht entschieden werden. Es ist jedoch anzunehmen, dass der Perthit-Zerfall der Kalifeldspate einerseits und die im mikroskopischen und submikroskopischen Grössenbereich deutlich erkennbare Kaolinisierung zu gewissen Argonverlusten führen. Es ist beabsichtigt, diese Frage weiter zu verfolgen.

Die erhaltenen Werte zeigen jedenfalls, dass die in den folgenden Versuchen an heterogenen Gesteinen gewonnenen Altersdaten *Mittelwerte* darstellen, *die sich aus den Altersdaten der einzelnen K-Minerale zusammensetzen.*

3. *Variskische Magmatite*

Zur weiteren Kontrolle der Methode wurde eine Serie von Gesteinen untersucht, deren Alter grössenordnungsmässig bekannt war und die sich dadurch auszeichneten, dass sie reichlich Grosskristalle von Kalifeldspat führen. Diese konnten daher leicht abgetrennt und für sich untersucht werden (ausser Nr. 3 d). Ausserdem wurden in jedem Falle Altersbestimmungen an einer unzerkleinerten, kompakten Gesteinsprobe vorgenommen, also einschliesslich aller nichtkalihaltigen Minerale (Quarz, Plagioklas u. a.).

Die Gesteine gehören sämtlich zur Gruppe der variskischen Magmatite des Schwarzwalds. Aus petrographischen Gründen werden der Wehra-Wiesental-Granodiorit und der Syenit von Vortal zu den älteren Intrusionen (mit starker Hybridisierung) gerechnet, der Albtal-Granit gehört in eine mittlere Phase (normal differenzierte, nichthybride Granite), der Granitporphyr in die vulkanitische Nachphase dieser Intrusionen.

Material	Lfd. Nr.	% K	mm^3 rad. A^{40} / g. Material	mm^3 rad. A^{40} / gr. K	Alter (10^6a)
(a) Granitporphyr (Geisbaumhalde)	204	4,30	0,0497	1,155	*276*
	214	4,22	0,046	1,10	264
	23	4,15	0,0456	1,10	264
Kfs. aus Granitporphyr	516	10,89	0,119	1,09	*262*
	15	10,25	0,111	1,08	260,5
	2	9,96	0,107	1,075	260
	17	10,27	0,105	1,02	246
	16	10,23	0,100	0,976	236,5
(b) Albtalgranit (Tiefenstein)	220	7,89	0,0903	1,15	*275,5*
	4	6,85	0,0783	1,142	273,5
	9	6,70	0,0718	1,072	258
Kfs. Grosskristalle aus Albtalgranit	1	9,55	0,116	1,218	*290*
	14	9,84	0,119	1,212	289,5
	13	10,23	0,123	1,202	287
	506	10,40	1,121	1,165	280
(c) Wehrawiesentalgranit, ohne Feldspatgrosskristalle (Burstel-Holzschlag)	584	3,87	0,0492	1,27	*302*
	21	2,07	0,0203	0,981	237,5
	60	1,75	0,0172	0,980	237
	20	2,44	0,0238	0,976	236,5
	7	2,32	0,01825	0,786	193
Kfs.-Grosskristalle des Granodiorit	63	9,58	0,11	1,15	*275*
	212	9,48	0,1082	1,14	273
	205	9,64	0,1085	1,128	270
(d) Syenit (Vortal b. Schenkenzell)	229	2,91	0,0376	1,293	306,5
	228	2,92	0,0376	1,29	306

Fundpunkte:

(a) Geisbaumhalde a. d. Strasse Bärental-Feldberg nö. Caritas.

(b) Stbr. südl. Tiefenstein, Albtal. westl. Flussufer.

(c) Erste Probe von Burstel, Wiesental zw. Schönan u. Mambach, übrige Proben von Holzschlag b. Burstel.

(d) Vortal b. Schenkenzell, Anbruch a. d. Kinzigbrücke

Aus den Zahlen der Tabelle ergibt sich, dass die Einzelwerte jeder Untersuchungsreihe im Durchschnitt mit etwa ± 10 Mill.J. ($= \pm 4\%$) um den Mittelwert streuen. Diese Streuung ergibt sich z.T. aus der Ungenauigkeit der Mess-

methode (Messgenauigkeit der A-Messung etwa 3–4% bei Mengen von 0,1–0,5 mm³ und 2% bei 0,5–10 mm³, Messgenauigkeit der K-Bestimmung im Mittel ±0,8%). Sie erklärt sich weiterhin aus unterschiedlichen A-Verlusten durch Umwandlung der K-Minerale, hauptsächlich durch partielle Kaolinisierung des Kalifeldspat und Chloritisierung des Biotit. Diese Verluste sind bei Anwendung von Messmethoden mittels radiogener *Gase* bekanntlich unvermeidlich (He-Methode!), sie sind aber wegen des grösseren Atomradius bei A kleiner als bei He. *Aus diesem Grunde sind die ermittelten Maximalwerte wahrscheinlicher als die errechneten Mittelwerte.*

Insgesamt variieren die Werte zwischen 193 und 306 Mill. J. (Maximalwerte zwischen 275 und 306 Mill.J.). Legt man als Vergleichsmaßstab die Zeitskala (A) von Holmes (1947) zu Grunde, so umfassen diese Zahlen den Zeitraum zwischen Ober-Devon (etwa 300) und Unter-Perm (etwa 200 Mill.J.) mit dem *Hauptgewicht im Unterkarbon* (etwa 280–250 Mill.J.). Das stimmt mit der bisherigen Auffassung des Alters der variskischen magmatischen Tätigkeit im Schwarzwald gut überein.

Dagegen zeigen die Werte, dass im einzelnen auch mancherlei Abweichungen vorkommen. So liegen die Werte für die Analysen der Gesamtgesteine und der einzelnen analysierten Kalifeldspate z.T. erheblich auseinander. Eine Erklärung für diese Beobachtung ist vorläufig schwer zu geben. Wie weit ein tatsächlicher Altersunterschied vorliegt, ist zweifelhaft (Einsprenglinge im Granitporphyr "jünger" als Gesamtgestein, Grosskristalle im Albtalgranit "älter" als Gesamtgestein). Es sei hier verwiesen auf Vorversuche (s.S. 4), die bei sorgfältiger Präparierung von Glimmer und Kalifeldspat des gleichen Gesteins bereits "Altersunterschiede" von ±10 Mill.J. ergeben haben. Hier müssen noch systematisch Versuche angesetzt werden, um die verschiedenen Einflüsse zu klären.

4. *Blastite nach Para- und Mischgneisen*

Wie Verfasser kürzlich näher ausgeführt hat (Mehnert 1957) führt eine *blastische Umkristallisation* zur Ausbildung charakteristischer Gefügemerkmale im metamorphen Grundgebirge des Schwarzwaldes. Sie ist als relativ niedrigtemperierte Vorphase der "Granitisation" (s.Absatz 5) anzusehen, wobei die regionale Plagioklas-Blastese unter niedriger temperierten Bedingungen, die Kalifeldspat-Blastese unter höher temperierten Bedingungen erfolgte.

Für beide Arten wurde je ein Beispiel ausgewählt. Das absolute Alter dieser Gesteine war bisher nicht bekannt, jedoch wurde die Kalifeldspat-Blastese altersmässig den frühen variskischen Granitintrusionen zugeschrieben (Hoenes 1940, 1949). Die Werte liegen im Bereich der unter Pkt. 3 beschriebenen variskischen Magmatite. Die seitherige Annahme eines frühvariskischen Alters der (Kalifeldspat-) Blastese ist also offensichtlich gerechtfertigt.

Die Werte für den Plagioklas-Blastit nach Mischgneis vom Artenberg liegen dagegen erstaunlich niedrig, da die Plagioklas-Blastese auf Grund der petrographischen Strukturen als älter angesehen wurde. Diese Diskrepanz ist vorläufig noch ungeklärt.

5. *Paragneise, Orthogneise und deren Granitisationsprodukte*

Das *absolute Alter des metamorphen Grundgebirges* des Schwarzwaldes war bisher nicht bekannt. Die *relative* Altersfolge ist in Arbeiten von Hoenes und Mehnert

Material	Lfd. Nr.	% K	mm^3 rad. A^{40} / g. Material	mm^3 rad. A^{40} / gr. K	Alter (10^6a)
(a) Kalifeldspat-Blastit nach Devonschiefer (Utzenfeld)	5	4,58	0,061	1,33	*314*
	201	4,47	0,057	1,272	302,5
	213	4,37	0,0534	1,22	291
Kfs. Megablasten aus diesem Gestein	208	5,91	0,071	1,20	*288*
	211	6,01	0,070	1,17	280
	202	5,75	0,0655	1,14	273
(b) Mischgneis-Blastit (Artenberg)	225	2,43	0,02665	1,09	*262*
	224	2,33	0,0249	1,07	258

Fundpunkte:
(a) Utzenfeld, Ortsausgang nach Wieden.
(b) Stbr. Artenberg b. Steinach.

(1949) mehrfach dargestellt worden, jedoch war über den Rhythmus der genetisch unterscheidbaren Phasen, d.h. ihre Zuordnung zu einer bestimmten Orogenese nichts auszusagen.

Hierbei ist folgendes grundsätzlich wichtig: *Die Auswahl des Probematerials für Altersbestimmungen* muss davon ausgehen, dass das gesamte metamorphe Gesteinsmaterial von einer regionalen Mobilisation ("Granitisation") betroffen worden ist, die das ursprüngliche Gefüge mehr oder weniger vollständig verändert hat. Es wurden daher nach Möglichkeit *reliktische* Gesteinspartien ausgewählt, um den Einfluss dieser Gefügeumwandlung auszuschalten oder wenigstens herabzudrücken. Wie die folgenden Werte zeigen, ist das nur z.T. gelungen: absolute Relikte sind offenbar altersmässig nicht erfasst worden. Die Werte streuen ausserdem erheblich stärker als die bisherigen.

Der Grauwackengneis vom Frohnbachtal stammt aus einer mehr oder weniger reliktischen, feinkörnig-quarzitischen Bank innerhalb stark mobilisierter Paragneise. Der Paragneis von Oberwinden ist lagenweise feinkörnig-blastisch, andere Lagen sind schiefrig und mit pegmatoiden Metatekten durchsetzt. Der Paragneis der Holzschlägermatte ist weitgehend diatektisch mobilisiert und hat einen massig granitoiden Charakter. Es handelt sich also um Gesteine mit erheblich komplizierterer Geschichte als die unter (3) beschriebenen Magmatite. Die allgemeine Mobilisation des Gefüges bewirkte eine Änderung des radiogenen A-Gehaltes der K-Minerale. Massgeblich für den A-Gehalt ist die *Letztkristallisation*, die also ein *Mindestalter* des betreffenden Gesteins wiedergibt. Diese Letztkristallisation ist bei den obenangeführten Gesteinen (wenn man von diaphthoritischen Umbildungen absieht) am *Ende der Granitisationspase* eingetreten, d.h. bei der Kristallisation der pegmatoiden und granitoiden Mobilisate.

Material	Lfd. Nr	% K	mm^3 rad. A^{40} / g. Material	mm^3 rad. A^{40} / gr. k	Alter (10^6a)
(a) Grauwacken-Paragneis feinkörnig, reliktisch (Frohnbach)	47	2,06	0,0318	1,545	*362*
	48	2,28	0,0276	1,21	289
	216	2,08	0,0226	1,09	262
	51	2,21	0,022	0,995	240
	50	2,25	0,0187	0,832	203
	61	2,20	0,016	0,728	179
(b) Grauwacken-Paragneis feinblastisch umkristallisiert (Oberwinden)	49	3,32	0,0451	1,358	*321*
	217	3,13	0,0402	1,265	302
	52	3,18	0,0372	1,17	280
	53	3,36	0,0385	1,15	275,5
	62	3,02	0,026	0,86	210
(c) Paragneis schiefrig, metatektisch (Oberwinden)	33	2,35	0,0353	1,50	*351*
	209	2,47	0,0366	1,48	347,5
	221	2,14	0,0304	1,42	335
(d) Paragneis massig, diatektisch (Holzschlägermatte)	203	2,21	0,0288	1,30	*308*
	207	2,17	0,0278	1,28	303,5
	219	2,03	0,0256	1,26	300
(e) Kinzigit (Schenkenzell)	227	2,25	0,027	1,20	*286*
	55	2,44	0,029	1,19	284,5
	54	2,27	0,0263	1,16	278
(f) Orthogneis (Einetwald)	222	1,74	0,0245	1,41	*332*
	223	1,94	0,0254	1,30	308
	521	1,87	0,023	1,23	291

Fundpunkte:
(a) Vorderes Frohnbachtal, Ortsausgang Oberwolfach
(b,c) Anbruch 300 m nordöstlich Oberwinden
(d) Felsgruppe 100 m westnordwestlich Holzschlägermatte, Bl. Freiburg
(e) Anbruch gegenüber Deckerhäusle, Tal der Kl. Kinzig, nördl. Schenkenzell
(f) Felswand südwestlich Einetwald, südöstlich Steinach, Kinzigtal.

Aus der starken Streuung der Werte im Vergleich zu den Magmatiten ist jedoch zu entnehmen, dass hierbei nicht das gesamte radiogene Argon abgegeben wurde, Das jetzt gefundene ^{40}A stammt also nicht nur aus dem Zerfallsprozess seit der Letztkristallisation, sondern enthält auch einen Teil des älteren, vor der Letztkristallisation entstandenen Argons. So stellen die jetzt ermittelten Werte

offenbar einen *Mittelwert* dar aus dem Alter des Ausgangsmaterials und dem Alter der Letztkristallisation. Anders ausgedrückt: die Werte sind offenbar durch den bei der Letztkristallisation (Granitisation) eingetretenen A-Verlust zu kleineren Werten hin verschoben. Eine gewisse Altersfolge ist auch bei diesen "verkürzten" Werten noch erkennbar, jedoch streuen die Werte zu stark, um dieses "verkürzte" Altersverhältnis genetisch für das *Ausgangsmaterial* auszuwerten. Es muss noch mehr nach *Relikten* gesucht werden, die durch die Granitisation möglichst wenig beeinflusst worden sind.

Ergebnis: Deutung der Alterswerte.

Die Argon-Kalium-Methode liefert wie alle auf radiogenen Gasen basierenden Altersbestimmungsmethoden *grundsätzlich zu kleine Werte.* D.h. die gefundenen Messwerte bilden eine Reihe, deren *Maximalwert* (innerhalb der apparativ bedingten Fehlergrenze von etwa $\pm 4\%$) dem wahren Wert am nächsten kommt. So liegen die Werte für die *pegmatitischen Nachschübe* der variskischen Granite mit etwa 250 Mill.J. nach der Zeitskala A von Holmes (1947) etwa an der Wende Unter/Oberkarbon. Das Alter dieser Nachschübe wurde zwar bisher eher für oberkarbonisch gehalten, jedoch ist keine sichere Beweisführung dafür möglich. Die Tatsache, dass die Werte eine *relativ geringe Streuung* zeigen, weist offenbar darauf hin, dass ins Gewicht fallende *Argonverluste nicht eingetreten sind.* Diese Werte sind daher gleichzeitig ein Beweis für die *grundsätzliche Brauchbarkeit der Methode.*

Die Reihe der variskischen Magmatite zeigt eine etwas grössere Streuung der Werte. Hält man sich an die ermittelten Maximalwerte, so hat die Reihe ein Alter von 260–300 Mill.J. Das entspricht nach der Holmes-Skala etwa einem Bereich vom oberen Devon bis zur Wende Unter-Oberkarbon. Die bisherige geologische Altersdatierung dieser Gesteinsgruppe ergab nach Wilser-Bubnoff-Hoenes etwa die gleiche Zeitspanne, d.h. die ältesten (hybrid-palingenen) Intrusionen wurden ins Oberdevon, die Hauptintrusionen ins Unterkarbon (Tournai-Visé) und die jüngsten Intrusionen der Zweiglimmergranite und der granitporphyrischen Nachschübe an die Grenze Unter-Oberkarbon bzw. ins Oberkarbon gelegt. Die *absoluten Alterswerte der variskischen Magmatite entsprechen also im wesentlichen der seitherigen geologischen Einordnung.*

Das Alter der *Metamorphite* und ihrer *Granitisationsprodukte* war bisher nicht bekannt. Aus Analogieschlüssen wurde für das *Ausgangsmaterial der Paragneise* vom Verf. (1953) ein präkambrisches Alter angenommen. Das Alter der Metamorphose und vor allem das der Granitisation war jedoch unsicher. Einerseits sprachen gewichtige Gründe dafür, die Granitisation für prävariskisch zu halten (petrographischer Gegensatz der granitisierten Gneise gegenüber den unmetamorphen Sedimenten der Oberdevon-Kulmzone), andererseits sind lückenlose Übergänge vorhanden zwischen den höchstmobilisierten Paragneisen (granitoide Diatexite) und den hybriden bzw. palingenen Erstintrusionen der frühvariskischen Magmatite ("Syenite" vom Erzenbachtyp, Syntexite der Wehra-Wiesentalzone). Diese Diskrepanz führte Hoenes und Mehnert (1949 ff.) dazu, Angaben über das mutmassliche Alter der Granitisation zurückzustellen, bis absolute Altersbestimmungen vorliegen.

Die Maximalwerte der bis jetzt vorliegenden Bestimmungen ergeben ein Alter

von 280–360 Mill.J. Dabei ist festzustellen, dass die Daten der reliktischen Paragneise (z.B. 5a mit 362 Mill.J.) ein Alter angeben, das durch den Argonverlust während der Granitisation (s.S. 6) "verkürzt" erscheint. Die Verkürzung ist desto grösser, je stärker die Mobilisation während der Granitisation war, d.h. je mehr primäres Argon während der Mobilisation entfernt worden ist. Daher zeigen die granitisierten Gneise (5 —b— f) geringere Werte (350–280 Mill.J.). Die am stärksten durch Granitisation veränderten Gesteine (z.B. 5d mit 300 Mill.J.) schliessen altersmässig an die ältesten frühvariskischen hybriden bis palingenen Magmatite (z.B. 3c,d S. 4) an. Damit ist die obengestellte Frage nach dem Alter der Granitisation zugunsten der 2. Annahme beantwortet, d.h. die *regionale Granitisation des Schwarzwälder Grundgebirges ist als Vorläufer der ältesten variskischen Magmenintrusionen anzusehen und dürfte nach den vorliegenden Altersdaten etwa in das Oberdevon, spätestens in die Wende Oberdevon/Kulm zu legen sein.*

Es erhebt sich am Schluss die Frage, ob über das *Alter des Ausgangsmaterials* der Metamorphite und Migmatite etwas ausgesagt werden kann. Bisher sind Gesteine mit einem höheren Alterswert als 362 Mill.J. nicht ermittelt worden. Da diese Werte jedoch durch Argonverluste während der frühvariskischen Granitisation "verkürzt" sind, ist anzunehmen, dass das Ausgangsmaterial der Paragneise zum mindesten älter als diese älteste bisher gefundene Zahl ist. Es sprechen mancherlei petrographische Gründe dafür (Hoenes & Mehnert, 1949), dass die Metamorphose der Para- und Orthogneise und ihre Verknetung zu heterogenen und homogenen Mischgneisen *erheblich älter* ist als die spätere Granitisation. Gegen die Annahme einer regionalen präkambrischen (assyntischen?) Metamorphose evtl. unter Mobilisation von palingenem magmatischem Material ist also aus den vorliegenden Altersbestimmungen heraus nichts einzuwenden. Das Alter der grauwackenartigen Paragneise als vermutlich algonkisch (Mehnert, 1953) könnte dann ebenfalls bestehen bleiben.

Die Untersuchungen wurden durch eine Sachbeihilfe der Deutschen Forschungsgemeinschaft unterstützt.

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Analyses of cosmic spherules with an X-ray microanalyser

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Abstract—With an X-ray microanalyser it has been possible to analyse different layers of cosmic spherules from deep-sea sediments, although the weight of each spherule was less than 10^{-6} g. A short description of the instrument is given. The spherules consist of iron oxides, with or without a metallic nucleus of iron–nickel–cobalt. Nickel and cobalt are strongly enriched in the nucleus (as much as 50% Ni has been found), which seems to be due to selective oxidation of the iron. Selective oxidation of different elements in steel as investigated with the microanalyser by Moreau and Cagnet (1957) is discussed in connexion with Prior's "law" concerning chondritic meteorites.

The much debated cosmic spherules of Murray (1876) have been thoroughly sought for in the sediments collected by the Swedish Deep-Sea Expedition, and it was also tried to determine the number per kilogram in different types of sediments (Pettersson, 1955; Pettersson and Fredriksson, 1958). Some microscopic investigations of the spherules have also been carried out (Fredriksson, 1956).

In order to prove definitely the cosmic origin of the spherules, some samples were analysed by Hecht and Patzak (1957). The Fe : Ni ratio was found to be 100 : 6 in one case and in another sample it was 100 : 15. Cobalt was also found. Later on some much smaller samples were analysed by Smales, Mapper and Wood (1958), who proved that the ratios Ni : Fe, Ni : Co and Ni : Cu of the spherules from deep-sea sediments were in good agreement with the average values of iron meteorites. However, analyses of the same elements in spherules collected from the air and suspected to be "cosmic" gave quite different values, and hence these spherules were probably artificial.

Although the average composition of the cosmic spherules was then known and their origin was considered proved, it seemed worthwhile to try to obtain some more information on the individual spherules than had been obtained by the microscope, which had only revealed iron oxide with or without a metallic nucleus (Fredriksson, 1956). The only remaining possibility was to make use of the X-ray microanalyzer (Castaing and Guinier, 1949, 1953; Castaing, 1951, 1956; Castaing and Descamps, 1955). This instrument makes possible analyses of selected areas in the order of 1 μ^2 on the surface of a polished sample. In short, it works as follows: An electron beam is focused on the surface of the sample by means of magnetic lenses. The electrons penetrate the sample down to about 2 μ and cause the sample to emit X-rays characteristic of the atoms present in the irradiated volume. The X-rays are analysed in a curved-crystal spectrometer; by measuring the wavelength and intensity of the characteristic rays, any point of the sample may be analysed quantitatively as well as qualitatively. The instrument can be used for all elements heavier than sodium. Further advantages are that the sample is not destroyed and that it can be observed during the analysis by

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means of a reflecting objective, through which the electron beam passes. Two analysers were built in 1955 by the "Office National d'Etudes et de Recherches Aéronautiques", Châtillon-sous-Bagneux, France, one of which is now operating at the "Institut de Recherches de la Sidérurgie", Saint-Germain-en-Laye. The authors wish to thank the Office National d'Etudes et de Recherches Aéronautiques for permission to use the microanalyser for this particular problem.

The spherules came partly from red clay from the Pacific (at least 100,000 years old) and partly from a so-called manganese crust. They had diameters varying from about 50 to 60 μ and had to be mounted in amalgam or plastic before polishing. Fig. 1 shows a spherule, *A*, with a metallic nucleus in which nickel was analysed at the six points I–VI. At point I, the content of iron and cobalt was obtained as well. At the same time another spherule, *B*, about 60 μ in diameter and also with a metallic nucleus, was analysed by Madame Bizouard and Dr. J. Philibert at the "Institut de Recherche de la Siderurgie", St. Germain-en-Laye. The results of these analyses are given in Table 1.

It must be emphasized that the content not only of Ni, but also of Fe and Co is fairly constant both in the "shell" and the core. This fact was easily verified by moving the sample under the electron probe, and watching the needle of a galvanometer, the deflection of which is nearly proportional to the concentration. Other elements than Ni, Co and Fe were also sought for, simply by searching the X-ray spectrum. However, nothing was found, i.e. there was certainly no heavy element other than Ni, Co and Fe present in concentrations above 1 per cent.

The values of spherule *B* permit a calculation of the ratios Ni : Fe and Ni : Co. Assuming the nucleus to have one-third to one-half of the total diameter, the specific gravity of the nickel–iron to be 8 and of the oxide shell 5, we find for the whole spherule Ni : Fe = 0·06 to 0·14 and Ni : Co = 11 to 20. Assuming the shell of spherule *A* to be magnetite with 0·1% Ni and the same amount of Co, we find Ni : Fe = 0·12 and Ni : Co = 17 (The diameter of *A* was 55 μ and of its nucleus $\sim$32 μ, Fig. 1). These values agree very well with those found in the earlier analyses mentioned above, and with the average for meteoric irons.

Two more spherules were analysed, both of which under the microscope seemed to consist of oxides exclusively. Figs. 2 and 3 show these spherules, and indicate the points where the analyses were made. The results are given in Table 2.

In spherule *C* it was observed that the Ni content decreased out from the centre of the dark area (see Fig. 2), but it was always much higher than in the surrounding light parts, where the iron content corresponds to a mixture of Fe_3O_4 (magnetite) and FeO. If it is assumed that the iron in the central part is present as magnetite (Fe_3O_4), most of the nickel must occur as very minute metallic spots. The iron content of the outer part of spherule *D* corresponds to magnetite, while the content of Ni and Fe in the nucleus is not far from that of $NiFe_2O_4$ ("trevorite")* in which Ni : Fe : O is about 27 : 51 : 22. The spherules *A*, *C* and *D* were extracted from a manganese crust and may have been rather well protected, while the spherule *B* was taken from an old red clay where it had been in

* Moreau and Benard (1953) report the formation of compounds such as $FeCr_2O_4$, $NiCr_2O_4$ and $NiAl_2O_4$ with spinel structure in alloys of Fe or Ni with a few per cent of Cr or Al, the alloys having been oxidized at temperatures between 800 and 1300°C.

contact with sea-water in an oxidizing environment. This fact may explain the rather low iron content in the shell of *B*, about 61 per cent, which may be obtained if part of the iron of the original magnetite became oxidized and hydrolysed.

Except for the inner parts of spherules *C* and *D*, the iron oxides contain only very small amounts of Ni and Co, and there is a tendency for Co to have been

Table 1. Analyses of two cosmic spherules consisting of an iron oxide shell with a metallic nucleus

Spherule	Analysed part		Element (%)			
			Ni	Co	Fe	Sum
A	Metallic nucleus	I	30·1	1·5	68·6	100·2
		II	29·8	—	—	—
		III	31·6	—	—	—
		IV	30·6	—	—	—
		V	30·3	—	—	—
	Oxide shell	VI	~0·1	—	—	—
*B**	Metallic nucleus		53·5	1·8 (4)	44·4	99·7
	Oxide shell		~0·2	~0·2	~61	—

* Analysed with an X-ray microanalyser at the "Institut de Recherche de la Siderurgie, Dep. Physique, St. Germain-en-Laye, by Madame Bizouard and Dr. J. Philibert. The authors also wish to thank Prof. C. Crussard for permission to publish the results.

Table 2. Analyses of two cosmic spherules consisting of oxides

Spherule	Analysed part	Element (%)	
		Ni	Fe
C	I	~20	~57
	II	<0·5	~75
	III	<0·5	~75
D	I	~24	≳40
	II	<1	≳70

somewhat enriched relative to Ni, which is in accordance with the redox potentials of the three elements. Obviously the spherules must have been melted to allow the nickel to concentrate in the metallic nucleus during the formation of the nickel-poor oxides, i.e. the spherules were formed during the flight through the atmosphere, where they reach high temperatures for a very short time, and they are not the result of a secondary oxidation of nickel–iron particles. M. Cagnet has remarked (personal communication) that a considerable concentration of Ni could be obtained at temperatures well below the melting point, provided the time is long enough (see also below). However, he also pointed out that a total

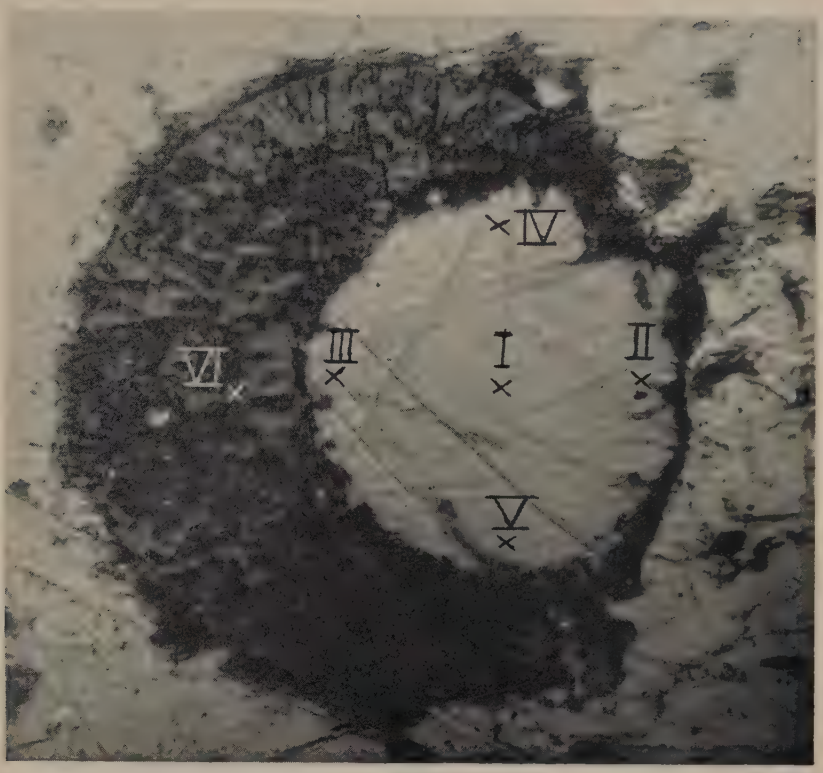

Fig. 1. Spherule *A*, diameter 55 μ. Metallic nucleus, white, with an oxide shell. I–IV analysed points, see Table 1.

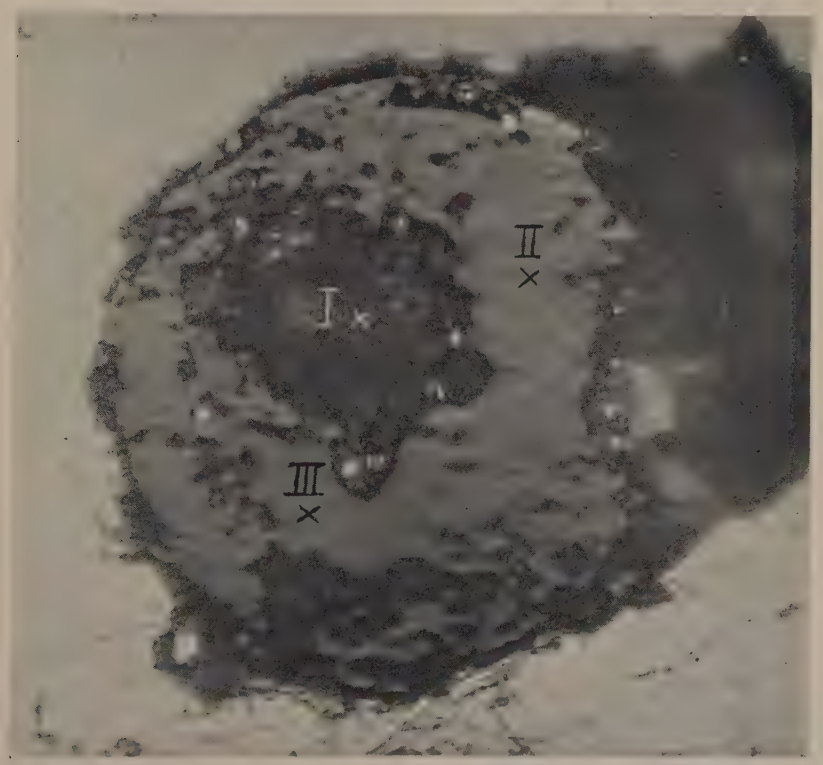

Fig. 2. Spherule *C*, diameter 50 μ. I–III analysed points, see Table 2.

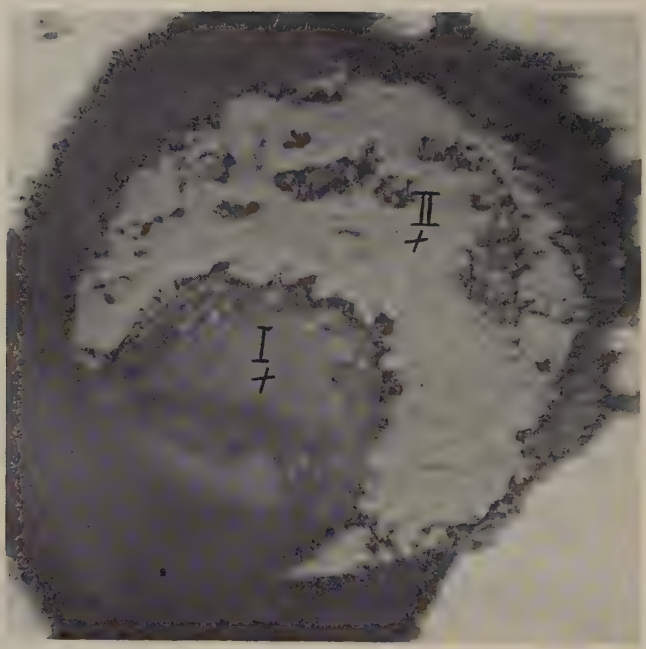

Fig. 3. Spherule *D*, diameter 60 μ. I–II analysed points, see Table 2.

absence of internal oxide in the metallic nucleus would favour the liquid explanation, and in fact no signs of an oxidation of the metal of spherules *A* and *B*, Table 1, could be observed. It might be a possibility that some of the spherules originate from small iron meteorites, but then these meteorites must have very low velocities, because they would otherwise be completely vaporized by the friction in the atmosphere. However, it seems most probable that the spherules form as drops drawn off from bigger meteorites by the friction against the air, especially since large amounts of spherules have been found in connexion with the fall of the big iron meteorite, e.g. Sichote Alin (Krinov and Fonton, 1954; Fessenkov, 1955). Fessenkov estimated the amount of particles which formed the tail of this meteorite to be almost 200 tons, i.e. much more than could actually be collected from the meteorite. This apparently supports the estimate made by Pettersson and Fredriksson (1958), who calculated the accumulation of black magnetic "cosmic" spherules to the earth to be 1000–5000 tons/year from the content of spherules in deep-sea sediments.

Finally, an investigation by Moreau and Cagnet (1957), which was also made possible by the X-ray microanalyser, will be mentioned. By oxidizing (at about 1200°C) the surface of a steel which contained, *inter alia*, 0·22% Ni, 0·31% Si, 0·62% Mn and 0·146% Cu, they found that, under the uppermost oxide layers, there formed a thin zone of FeO, $(Fe,Mn)_2SiO_4$ (manganese-bearing fayalite), and small spots of metal with 96% Fe, 3% Ni and 0·75% Cu, i.e. both Ni and Cu had been strongly enriched; Ni more than ten times. These interesting results may have an important bearing on the processes discussed above and, furthermore, on Prior's "law" concerning the Ni : Fe ratio of metal phases and silicate phases of stony meteorites.

Obviously the X-ray microanalyser is a most useful tool not only in metallurgy but also for many mineralogical problems, and it seems to provide possibilities for solving a lot of the intricate problems involved in the relations of different mineral phases in meteorites, and in the separate chondrules of the chondrites.

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Thorium in iron meteorites: a preliminary investigation*

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Abstract—By means of neutron activation analysis, thorium concentrations in two iron meteorites have been found in the approximate range of from 6×10^{-12} to 20×10^{-12} g Th/g meteorite. These values are lower by at least two orders of magnitude than previously determined levels of thorium concentration in irons. It is possible that the wide divergence of results must be attributed to differences in method, and evidence is presented in support of the validity of the method of neutron activation analysis.

If Urey's calculated value for the distribution coefficient of thorium between iron and silicate phases is correct, the present thorium data seem to further substantiate the view that thorium in irons occurs primarily in inclusions or in thorium compounds dissolved in the iron. Comparison with uranium concentrations in irons recently determined by neutron activation analysis suggests moreover that if the thorium is accounted for by inclusions, these inclusions are not primarily silicate in nature; or if thorium is attributable to dissolved thorium compounds, the solubility of thorium compounds is less than that of uranium compounds in the original molten iron phase.

Introduction

An extensive investigation of thorium concentrations in iron meteorites by Dalton and co-workers (1953) yielded values ranging approximately from $<2 \times 10^{-9}$ to 100×10^{-9} g Th/g meteorite for twelve irons. These results were based on thoron activity measured in a continuous flow ionization chamber and on the α-activity of Bi^{212} determined by scintillation counting. In a later reference to these results, Professor H. C. Urey (1955) pointed out on theoretical grounds (having assumed the validity of Goldschmidt's theory for the distribution of elements between the silicate, troilite and metallic phases) that the concentrations of both uranium and thorium in a pure metallic phase should be extremely low and that the experimentally observed uranium and thorium must be attributed to silicate or sulphide inclusions in the irons. A further possibility accounting for the observed thorium stems from the fact that Urey's calculation assumes no solubility of thorium compounds of any kind in the iron. In a recent private communication Professor Urey observes that this assumption is probably untrue because of the increasing mutual solubility of substances at high temperatures, and that it is possible that thorium in metal meteorites is really dissolved in the iron phase as ThO, ThS, etc.

Reed and Turkevich (1955) found in an initial investigation that uranium concentrations in two iron meteorites determined by neutron activation analysis were lower by at least an order of magnitude than those obtained by Dalton *et al.* for the same meteorites. A continuing study of additional irons by Reed, Hamaguchi and Turkevich (in press) has yielded results consistent with their earlier findings. Previous work by the authors (Bate, Huizenga and Potratz, 1957), has established that thorium in chondrites bears essentially the same ratio to

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uranium (Hamaguchi, Reed and Turkevich, 1957) as is found in terrestrial silicates, and it was decided to make a preliminary investigation of thorium in irons to ascertain the magnitude of the Th/U ratio in the iron phase. Since neutron activation analysis for thorium (Jenkins, 1955) affords higher sensitivity and provides greater freedom from reagent contamination than any other known method, it was well suited for purposes of this investigation, with the availability of appropriate pile facilities.

Sample Preparation and Activation

Samples were sawn from the iron meteorites into small pieces approximately $3 \times 3 \times 15$ mm of about 1 g mass. Those pieces of greatest homogeneity were selected for activation and placed in quartz vials which were closed by ground quartz stoppers. A flux monitor for each sample vial was prepared by evaporating an aliquot of a standard thorium solution (to give $\sim$1 μg Th) in a small quartz tube which was subsequently sealed. The flux monitor was then placed next to the sample vial and wrapped in place with aluminium foil.

Two separate portions of Arispé and a sample of Sandia Mountains were thus prepared, each with its separate flux monitor, and wrapped together in aluminium foil. This sample package was placed with appropriate wadding of aluminium foil inside an aluminium can which was welded shut to form a watertight seal. As thus mounted, the three samples and flux monitors were all contained within a circle of 1 in. diameter and approximately in the same plane. These samples were irradiated together for a 3 week period in the Materials Testing Reactor at Arco, Idaho under a nominal slow neutron flux of 3×10^{14} neutrons cm^{-2} sec^{-1}.

Chemical Separation and Purification

For convenience (working time) of chemical processing radiochemical assay was based on protactinium-233, the 27·4 day daughter of the 23·3 min Th^{233} which is produced by neutron activation of Th^{232}. Chemical separation and purification of the Pa was made according to the procedure of Potratz and Bonner (1954) and was effected as follows:

Owing to the high activity (>25 r/hr at 2 in.) of the samples, all initial weighing and processing was done remotely behind radiation shielding. The sample was first etched in 6 N HCl, removing approximately 5 per cent of its mass in order to eliminate any possible surface contamination received during sample preparation and activation. After drying and weighing, the sample was transferred to a 40 ml polyethylene tube containing 15 ml of 8 N HCl, 1·5 ml of concentrated HF, and 30 mg of zirconium (as chloride) together with a known amount of Pa^{231} tracer (from 50 to 130 counts/min).

After a steady rate of hydrogen evolution was obtained the mixture was gradually heated to the boiling point, which consummated the dissolution process in about 20 min. (The sample dissolved much more rapidly in strong HNO_3, but Fe^{+3} was found to interfere with subsequent Pa separation.) The solution was held at the boiling point for 1 h to ensure isotopic equilibration of the Pa^{231} tracer with the Pa^{233}.

Transfer of the solution to a 40 ml lustroid tube was made (to permit visible

observation of precipitate), leaving behind any acid-insoluble residue,* followed by addition of 1 ml of concentrated HF and 5 ml of H_2O. Barium fluozirconate ($BaZrF_6$) was precipitated (coprecipitating Pa) on the addition of 120 mg of barium (as barium chloride) and after standing for 15 min, the mixture was centrifuged and the supernate discarded. The precipitate was washed in 10 ml of H_2O and the activity at this point was generally ~0·5 r/hr at 2 in.

The sample was transferred to a regular hood and taken through the following basic sequence. The barium fluozirconate precipitate was dissolved by treating with 3 ml of saturated H_3BO_3, 1 ml of concentrated HNO_3, and 2 ml of H_2O, followed by heating on the steam bath for several minutes. A 1 N solution (15 ml) of HIO_3 was added and the iodate precipitate (coprecipitating Pa) was allowed to stand for 5–10 min. After centrifuging, the precipitate was washed with H_2O and the supernate discarded. The iodate precipitate was dissolved by heating in 5 ml of concentrated HCl, followed by addition of 2 ml of H_2O and by continued heating until complete dissolution was obtained.

The solution was transferred to a 125 ml separatory funnel together with 30 ml of 6 N HCl. Solvent extraction into 35 ml of redistilled di*iso*propyl carbinol was effected by thorough shaking with the aqueous acid phase for several minutes. After drawing off and discarding the aqueous phase, the organic phase was washed with two 25 ml portions of 6 N HCl. The Pa was extracted back from the carbinol phase by treating with two 10 ml portions of a solution made by diluting 3 ml of concentrated HNO_3 and 0·5 ml of concentrated HF to 20 ml. To the combined aqueous extracts were added 2 ml of concentrated HF and 20 mg of zirconium (as zirconyl nitrate), and a lanthanum fluoride scavenge was then effected by adding 20 mg of lanthanum (nitrate solution). The LaF_3 precipitate was washed and discarded, the wash being retained with the supernate.

The basic sequence beginning with a barium fluozirconate precipitation was then repeated one or two more times, depending upon the purity of the protoactinium as determined by the gamma spectrum observed with the multichannel analyser. On the last cycle the dissolved iodate precipitate was taken up in only 10 ml of 6 N HCl and contacted with 10 ml of di*iso*propyl carbinol. After washing the carbinol with two 10 ml portions of 6 N HCl, the Pa was back-extracted into 0·8 ml of H_2O and 0·2 ml of concentrated HF. The aqueous phase was washed with two 5 ml portions of carbinol and mounted for counting on a Pt disk by evaporation under a heat lamp.

Excellent separation from the iron and all lesser activities was obtained with only two or three cycles of the basic sequence of purification described, at the same time affording good yields (40–70 per cent) as measured by final recovery of the tracer. Trial experiments using Pa^{233} and Pa^{231} tracers indicated satisfactory equilibration of the two isotopes in the chemical processing as described above.

Each flux monitor was recovered from its quartz tube with a minimum of chemical processing as follows. The flux monitor tube was washed with hot, strong HCl, dried and placed in a 40 ml polyethylene tube. The quartz tube was

* Insoluble residue (amounting to nearly 5 per cent of the sample) from the largest sample, Arispé II, was later processed for Pa. The residue dissolved readily in aqua regia. No Pa was found, and the residues from the remaining two samples were discarded, being proportionately much smaller in amount.

broken with a lucite rod and leached with a 2 ml portion of 6 N HCl containing about 0·1 ml of concentrated HF. The mixture was heated on the steam bath for several minutes and the acid decanted into a 10 ml volumetric flask. This leaching procedure was repeated four times with 2 ml of acid, and the total volume was brought to exactly 10 ml at room temperature. The entire solution was immediately transferred to a polyethlene bottle for storage, and at the same time several aliquot portions were micro-pipetted on to Pt disks for counting.

The glass fragments of one of the monitors remaining after the foregoing treatment were checked for activity in the following manner. The glass was dried and ground in a mortar and dissolved in concentrated HF, followed by fuming with concentrated $HClO_4$. The resulting solution when counted gave a high β^- activity, but its gamma spectrum showed less than 1 per cent of the activity of the flux monitor solution at 310 keV energy. This experiment was considered evidence of: (1) complete recovery of the Pa off the walls of the quartz tube into the flux monitor solution proper, and (2) absence of any appreciable Pa activity in the glass, and of other activities with gamma rays of comparable energies. The glass remaining after dissolution of the other flux monitors was therefore discarded without further treatment.

The flux monitors were examined for gamma rays with energies different from the Pa^{233} gamma rays. Thorium-232 is fissionable with fast neutrons ($\geqslant$1·1 MeV) and the possibility exists for detecting characteristic gamma rays of some of the fission products. If present, the intensities of such gamma rays were too low for detection. The gamma ray spectra of the flux monitors were experimentally identical with the Pa^{233} standard spectrum. In addition, the 100 and 310 keV gamma peaks of the flux monitors decayed with 27 day half-lives.

Unfortunately one of the flux monitor tubes was broken before removal from the irradiation can, but the activity recovered from the two unbroken monitors agreed to within 1 per cent. This agreement was in turn viewed as a demonstration of the uniformity of the neutron flux over the region of the samples, and also of the complete recovery of the Pa activity inside the two monitor tubes (if a fortuitous cancellation of two off-setting effects may be ruled out).

Results and Discussion

The results are shown in Table 1. The thorium concentrations are calculated for each sample on the basis of three different activities: (1) the 100 keV Pa^{233} gamma activity (the designation "gamma" is in this instance merely nominal since most of this radiation actually consists of U^{233} K X-rays), (2) the 310 keV Pa^{233} gamma activity, and (3) the gross β^- Pa^{233} activity, each referred to the corresponding activity of the flux monitor. The gamma activity was detected by means of a $2\frac{1}{2}$ in. NaI crystal, with the output of the photomultiplier tube fed into a 256-channel pulse height analyser. β-Counting was effected with an end-window proportional counter at about 33 per cent geometry, using a 5 mg/cm^2 Al absorber. The integrated gamma activities were from 30 to 50 counts/min against a corresponding background of about 50 counts/min and the gross β^- activities were from 20 to 90 counts/min above a β^- background of about 10 counts/min. In all cases the flux monitors were counted under the same geometry as the samples.

Table 1. Thorium concentration in iron meteorites by neutron activation analysis

Sample*	Thorium concentration (10^{-11} g Th/g sample)		
	100 keV γ	310 keV γ	Gross β^-
Arispé, Sample I	1·8	1·6	1·1
Arispé, Sample II	0·61	0·59	0·53
Sandia Mountains	1·0	1·1	0·89

* The authors are indebted to Dr. H. H. Ninninger of the American Meteorite Museum, Sedona, Arizona, for these samples.

The gamma spectrum of the Sandia Mountains sample is displayed in Fig. 1, together with that of the flux monitor. The sample activity has been corrected for background and for a small contribution from the tracer Pa^{231} activity. The

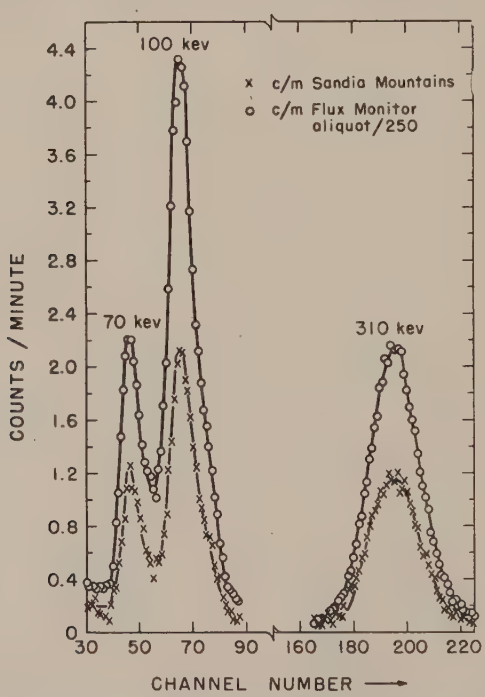

Fig. 1. Comparison of gamma spectrum of Sandia Mountains iron meteorite with that of flux monitor. Aliquot of flux monitor shown contained $2{\cdot}5 \times 10^{-9}$ g thorium. To obtain the counts/min. per channel of the flux monitor aliquot the counts/min on the ordinate are to be multiplied by 250 as indicated on the graph.

lowest energy line at about 70 keV (appearing as a "spur" on the 100 keV peak) is K X-ray radiation from the Pt disks on which both the sample and flux monitor were mounted. (This identification of the 70 keV peak was supported by its absence when the flux monitor was mounted on an aluminium plate before scintillation counting.) The two spectra are seen to be identical in form and the

identification of the Pa^{233} gamma activity is therefore considered very positive. The agreement (~10 per cent or less) of the thorium values for each sample in the table based on the two different gamma activities reflects the essential purity of the Pa^{233} gamma spectra obtained.

It may be noted in the table that for each sample the thorium concentration based on gross β^- activity is smaller than those calculated for the gamma activities. Although the β^- result for Arispé I seems unduly low, a plausible explanation for the consistently low β^- results is suppression of the true value by extraneous β^- activity in the flux monitor. As noted in earlier discussion, the quartz tubes containing the flux monitor were found to carry a large amount of β^- activity and no appreciable gamma activity corresponding to the energy of the Pa^{233} gammas. In the leaching process described, a small amount of quartz may have been dissolved with the flux monitor, thereby introducing extraneous β^- activity.

In view of the care taken to avoid and eliminate contamination of the samples, the variations shown between samples in the table are not considered attributable to contamination. The difference between the two samples of Arispé in particular is large compared to statistical errors associated with the counting times used and the variation between the two samples therefore appears to be real.

Unfortunately, the samples analysed in this investigation are different from those analysed by Dalton and co-workers, and a rigorous comparison of the diverse methods cannot be made. However, since most of the values found by Dalton *et al.*, are much higher than the concentrations obtained here (which are below the limits of accuracy reported by the British group), the relative validity of the methods must be examined if the possibility of a fortuitous (but real) variation of such magnitude is considered unlikely. Suppression of induced activity by neutron "self-shadowing" of the sample is a possible mechanism whereby apparently low thorium concentrations may be produced in the neutron activation analysis. This, however, is not regarded as a serious factor here for theoretical reasons (the capture cross-sections of the predominant iron nuclei are low and the sample dimensions are small), and because Reed and Turkevich (1955) have experimentally demonstrated the absence of appreciable self-shadowing effects in the case of uranium in iron.

Another possible cause of suppression of induced activity from thorium is thermal heating of the sample (relative to the flux monitor) during activation. Since the capture cross-section of thorium decreases with neutron energy (up to 20 eV), the amount of induced activity would be reduced with thermal heating if neutrons achieved thermal equilibrium with the sample locally. With thorium, however, the total capture cross-section decreases only by a factor of 3 as the neutron energy increases from 0·025 eV to 10 eV (Hughes and Harvey, 1955). Therefore, the reduction in activation of thorium in iron could not exceed a factor of 3 even if, in an extreme case, the iron were to reach its melting point (neutrons remaining in thermal equilibrium with the sample), and if the flux monitor remained at the temperature of the pile-cooling water. An effect approaching two orders of magnitude is not realized apart from resonance effects, which for thorium begin at 20 eV. It should be noted moreover, that for suppression of the final yield, resonance effects must take place primarily in the flux monitor and not in the sample.

But if such a peculiar resonance distribution were possible, the net effect should be small for a well moderated region of the pile since the number of neutrons with the required resonance energy should be small relative to the total flux of truly slow neutrons. In general, those factors which would introduce activation errors in the sample are largely eliminated by the use of flux monitors, and it is difficult to conceive of a mechanism whereby the apparent thorium content of a sample could be suppressed by as much as two orders of magnitude, in a properly monitored activation.

A final possible factor arising from activation procedure which would also lead to erroneously low thorium results is a rendering of the protactinium into a chemically inert or intractable form during activation. Protactinium behaviour during activation in a solid iron matrix at tracer concentrations cannot be definitively stated, but there is no cogent reason on the basis of present knowledge to admit exotic chemical effects by activation as a very real possibility.

Reed *et al.* (in press) find by neutron activation analysis uranium concentrations in five iron meteorites ranging from 3×10^{-11} to 10×10^{-11} g U/g sample, and for Arispé in particular they report upper limits ranging from 4×10^{-11} to 20×10^{-11} g U/g sample. It would seem that the thorium concentrations here reported are more compatible with these results than with the higher values given by the British group and with the similarly high uranium abundances in irons more recently reported also by Soviet investigators (Starik and Shats, 1956).

Conclusions

Further work is necessary to provide an adequate basis for rigorous generalizations, but this preliminary study would seem to support the following conclusions:

(1) A distribution coefficient of $\sim 10^{-4}$ for thorium in the metal phase to thorium in the silicate phase obtained with the data presented here and in earlier work (Bate *et al.*, 1957) more nearly accords with Urey's (1955) calculated value than do those coefficients obtained with thorium abundances determined previously by nonactivation methods of analysis.

(2) A thorium distribution coefficient of 10^{-4} is, however, still far in excess of Urey's calculated value of $3{\cdot}5 \times 10^{-16}$ and lends further support to Urey's suggestion that most of the uranium and thorium in irons occurs in inclusions or in dissolved uranium and thorium compounds.

(3) Comparison with the uranium concentrations in irons reported by Reed *et al.* (in press) suggests that in the metal phase thorium abundances may be lower than uranium abundances and in any event the Th/U ratio does not appear to be as large as the 4:1 ratio characteristic of chondrites. This situation would require the inclusion of a phase or phases other than silicate in which the Th/U ratio is less than that in chondrites; or a similar effect could be realized by preferential solubility of uranium compounds over thorium compounds in the metal phase. The tentative aspect of this third conclusion must be emphasized inasmuch as the apparently low Th/U ratio in irons may be accounted for by limitations in accuracy and by statistical fluctuations between portions of a given sample as noted above, for both uranium and thorium.

(4) As to method, it is believed that the uranium and thorium concentrations

in irons as obtained by neutron activation analysis are mutually compatible and therefore stand or fall together on the basis of the validity of the method of neutron activation analysis. The fact that compatible results are obtained with two different nuclear and chemical species would seem to argue against peculiarities in resonance effects or in chemical behaviour as the sources of possible error. If the method of neutron activation analysis is indeed in error, the cause must lie in some physical factor, or factors, of the activation process, as yet largely unknown or not well understood.

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A search for airborne particles of meteoritic origin

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Abstract—A year-long programme involving daily collections of atmospheric dust at several widely separated, isolated sites has been undertaken with the object of identifying particles that may be of extra-terrestrial origin. The particles in question are opaque, shiny spherules with diameters less than 15 μ. They appear to be of a nature entirely different from that of the larger spheres abounding in densely populated areas. Their meteoritic origin is suggested by recent evidence regarding ablation of meteorites and by the fact that the rate of fall and the frequency distribution with size of these particles have been found to be the same at the various stations. The average rate of fall for each station was 1·1 spherules greater than 3 μ in diameter/cm^2/day. Assuming that the density of the counted particles is that of magnetite, this rate corresponds to an annual accretion for the entire earth of about 5×10^8 kg of these particles.

The problem of collecting at the earth's surface small particles of matter which have entered the atmosphere from the outside is made difficult by the predominance in the air of terrestrial dust. A number of investigators (Buddhue, 1950; Crozier, 1956; Rudaux, 1930; Thomsen, 1953) have studied spherical, magnetic particles which they collected from the air, believing that such particles might be formed by the ablation of meteors. However, Hoppe and Zimmermann (1954), and Handy and Davidson (1955) have concluded that black magnetic spherules collected near industrial centers are nearly all terrestrial in origin.

Collections of atmospheric dust made in New Haven contain a very large number of spherical particles, some of which are relatively smooth, some rough-surfaced and some cindery. At Yale Observatory, very near the centre of the city, approximately 100 spherules larger than 5 μ in diameter were collected per cm^2/day. Most of these particles had diameters of about 25 μ. That they are predominantly industrial in origin is apparent from the fact that their number drops by a factor of 2 on Sundays, and by a factor of 4 at 10 miles from the centre of the city.

During 2 months of the summer of 1954 one of the authors (P. W. H.) obtained daily collections of atmospheric dust on Whidbey Island, 35 miles north of Seattle, Washington, at latitude 48°00′ N, longitude 122°22′ W. Incidental collections were made in three locations, all nearly 10,000 ft in altitude, on the slopes of Mount Rainier (65 miles south-east of Seattle at latitude 46°50′ N, longitude 121°45′ W). Comparisons of these two sets of observations indicated that spherical, shiny particles, less than 10 μ in diameter, fell from the atmosphere at both places at about the same rate.†

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† The recent collections by Crozier (unpublished work, personal communication, 1957) of magnetic spherules larger than 5 μ in diameter should be mentioned here. He has studied samples of dust collected at two sites in the San Mateo Mountains in New Mexico, differing in altitude by 6000 ft. The rates of fall and the size distribution of the spherules at the two collecting sites agree fairly well.

A crude test for magnetism was applied to the Whidbey Island spherules as follows. Shallow pans containing water served as collecting vessels for the test. After a week's collection an alnico magnet inserted in a test tube was slowly passed over the bottom of the pans to attract all magnetic particles. Those adhering to the bottom of the test tube were transferred by contact to a microscope slide. Examination of the particles so isolated did not reveal any difference in appearance from the particles described above, which were obtained by the standard collecting method to be described in the next section. It was therefore, thought worthwhile to establish whether or not such particles fell elsewhere at this same rate, especially at more isolated locations.

Technique of Sampling and Examination

In the present programme collections of atmospheric dust were concurrently made at three widely separated sites, each of which is remote from densely populated areas. These were the Smithsonian Astrophysical Observatory's Table Mountain Station above the Mojave Desert of California (latitude 34°30′ N, longitude 117° 30′ W), a field site of the Geophysical Institute in central Alaska (latitude 65° N. longitude 148° W), and the Meteorological Observing Station of the Meteorological Service of Canada at Resolute, Northwest Territory, on Cornwallis Island in the Arctic (latitude 75° N, longitude 95° W). The programme involved daily collections of atmospheric dust made simultaneously at these three stations for a period of 1 year, from July 1955 to June 1956.

Collections were omitted on days of rain or snow; occasionally they were spoiled by the formation of hoar frost on the slides. This trouble was avoided at the Alaskan station by the use of an open heating box during part of the winter months. Since the rate of collection of particles might be affected by this alteration of conditions, such data are marked by asterisks in Table 1. A delay in shipping prevented the Resolute station from beginning collections according to schedule and there is therefore a lack of data from this site for the first part of the year of collecting.

Each day glass microscope slides were covered with a slow-drying plastic cement, made by mixing ethyl cellulose (10 parts by weight), tricresyl phosphate (3 parts by weight) and tetrahydronapthalene (87 parts by weight). A number of unexposed slides covered with this material were scanned to test this adhesive cement for contamination by extraneous matter that might be mistaken for particles of the type under investigation. The slides were placed in an open tray at each collecting site and normally exposed for a period of 24 hr. At the end of the exposure each slide was covered with a second glass slide with a spacer inserted, and tightly sealed with tape. At Yale the slides were examined with a binocular microscope under a magnification of 500 diameters.

In order to hold down the labour of scanning to a reasonable fraction of the time available for the project, it was decided to examine only slides for every second day during periods when daily collections were made. However, during some periods when collections were missed owing to rain or other contingencies, all available slides were scanned.

Independent tests by a second observer with the same magnification showed that effectively all of the particles in question larger than 3 μ in diameter were

Table 1

Month	Total number of spherules discovered during each month			Efficiency of collection (collection time/total time in month) (%)			Computed daily rate of accretion (particles/cm^2)		
	California	Alaska	Canada	California	Alaska	Canada	California	Alaska	Canada
July 1955	32	4	—	71	30	—	1·4	0·5	—
August	16	1	—	40	17	—	1·3	0·2	—
September	11	10	—	43	18	—	0·8	1·6	—
October	15	2	—	42	8	—	1·2	0·5	—
November	6	0	—	29	9	—	0·9	0·0	—
December	3	5	—	30	10	—	0·3	3·0*	—
January 1956	18	1	—	26	11	—	2·2	0·3*	—
February	4	3	2	43	10	28	0·3	1·2*	0·3
March	8	29	11	42	48	27	0·5	1·8	1·4
April	4	74	7	23	65	20	0·3	4·2	1·1
May	29	8	0	36	47	7	1·3	0·5	0·0
June	35	6	6	47	27	27	1·2	0·9	0·8
July 1956	—	—	4	—	—	12	—	—	1·0

* Heating box used to prevent the formation of hoar frost (in Alaska only).

counted. Although smaller particles were sometimes found, these tests showed that they were often missed. For this reason the recorded particles with diameters smaller than this limit are not included in the following discussions.

In addition to opaque spherules, the slides contained numerous pollen grains and irregular transparent and opaque particles. Every object with a perfectly circular outline was examined with back lighting and side lighting and was tested for behaviour under polarized illumination. Only particles which were completely opaque, non-polarizing, and specularly reflecting were counted. These criteria were satisfied by all spherules found except five particles in the California collections which appeared dark red and glassy when illuminated from the side, and five large round objects, about 25 μ in diameter, from the same station. These had relatively rough surfaces, similar to the particles—believed to be of industrial origin—found in New Haven.

Description of samples and their evaluation

(1) The principal qualitative result of this programme is the fact that the collections at the three stations regularly contain spherules indistinguishable, by the criteria adopted, from those that had attracted attention in the samples of the preliminary programme carried out at Whidbey Island and Mount Rainier.

(2) According to Fig. 1, the frequency-size distributions at all three sites appear to be identical. It must be admitted that the total number of particles is smaller

than would be desired. Since the average time required for scanning 1 cm² on the slides was of the order of 1 hr, it proved impractical to obtain results of greater statistical significance by scanning a greater total area of the available samples.

Because of local weather conditions, the total number of slides examined at each station was not the same. Therefore the number of spherules examined from each station differed, 143 having been found in Alaskan collections, 171 in the Californian, and 26 in the Canadian.

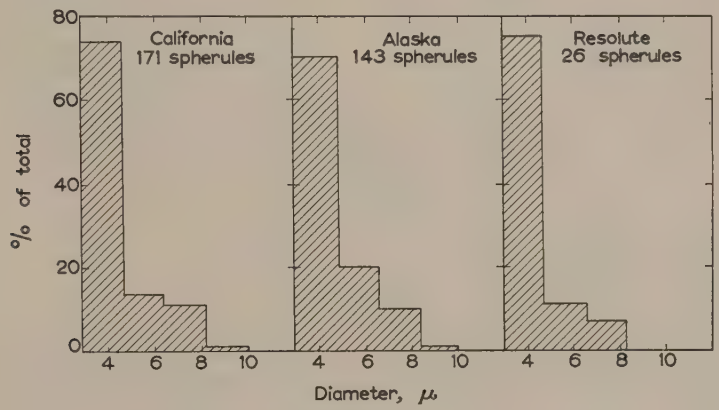

Fig. 1. Frequency-size distribution for spherules based on the totals of 143 spherules from Alaska, 171 from California, and 26 from Resolute.

Fig. 1 shows the size distribution of particles greater than the 3 μ diameter limit imposed upon the data by the scanning magnification used. In the total scanned area of 251 cm² and a total exposure time of 268 days, the only particles found which answer the description of those large spheres studied by Buddhue (1950) and Thomsen (1953) were the five California spherules mentioned in Section 1 of this report. These were larger (about 25 μ in diameter) and somewhat rough-surfaced under high magnification.

(3) The monthly variation of the rates of fall of the spherules is given in Table 1. Because of the small number of particles per area, short-term fluctuations in the rate of fall of the spherules are difficult to establish with the present data. Fig. 2, which for reasons of economy of space shows only the daily counts from April to June 1956, contains a conspicuous maximum count, occurring in Alaska around 12 April 1956. No other obvious peak was observed in the present programme, although such had turned up in the collections made on Whidbey Island in July 1954 (Fig. 3).

(4) From the total number of hours of exposure and the total number of particles larger than the 3 μ limit of certitude of recognition, the average rate of accretion at each station was computed. These values are shown in the table at the top of page 130.

For comparison the corresponding figure for the Whidbey Island collections, neglecting the single slide on which the unusual maximum count occurred, was 1·1. A glance at Fig. 1 will show that 75 per cent of the particles counted had diameters between 3 and 6 μ. Hence the average rate of fall computed above essentially

Collecting site	Rate of fall
Table Mountain, California	1·0 spherules per cm^2/day
Central Alaska	1·2 spherules per cm^2/day
Resolute Bay, Canada	1·1 spherules per cm^2/day

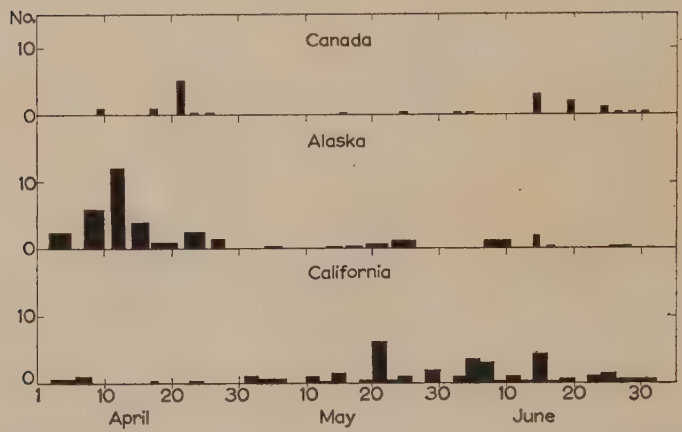

Fig. 2. Numbers of spherules/cm^2/day in the collections during spring 1956. Blank spaces mostly represent lack of samples due to snow or rain; for monthly "efficiency" of collection compare Table 1.

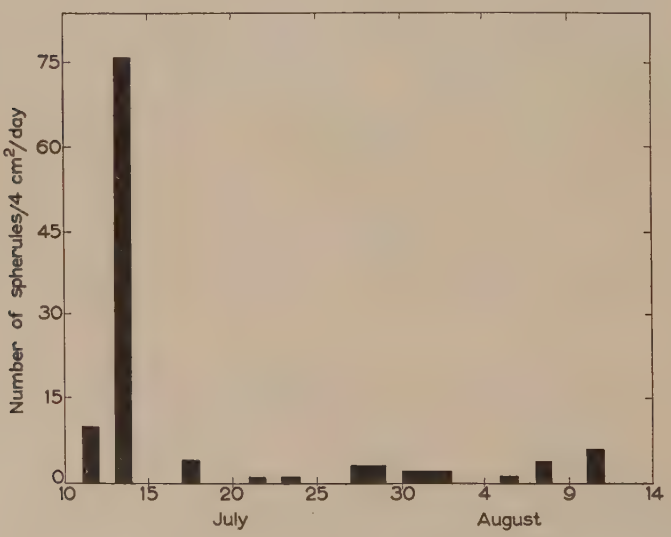

Fig. 3. Daily variation in the numbers of spherules collected at Whidbey Island during summer 1954.

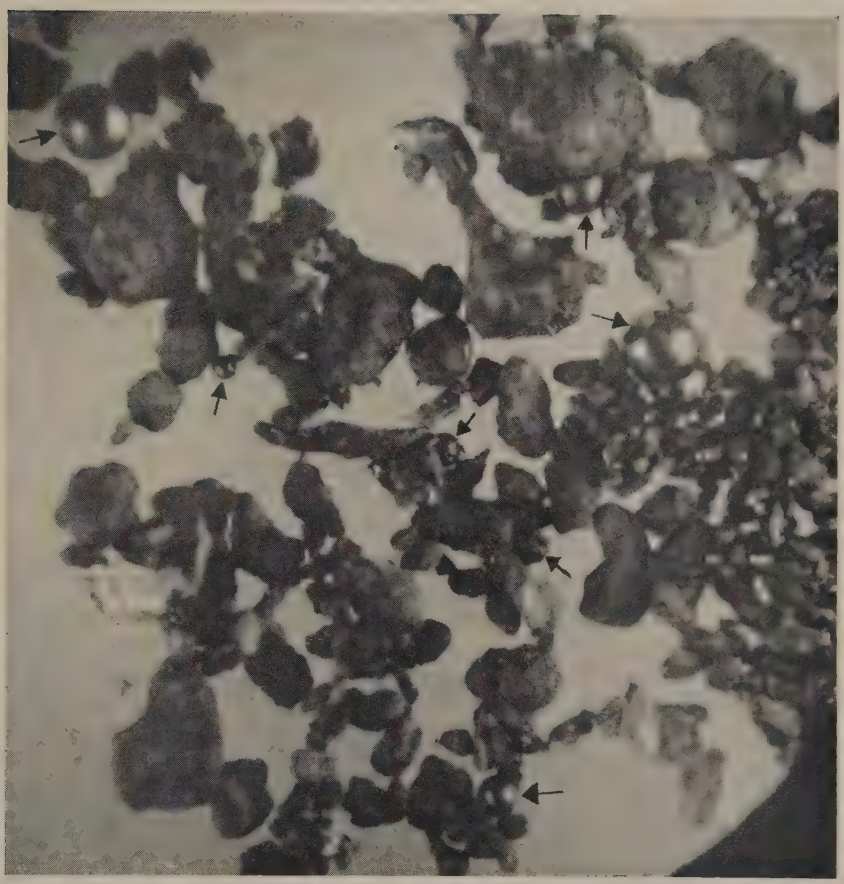

Fig. 4. Particles of magnetic dust from the soil at the site of the Sikhote-Alin meteorite fall. ×100.

Fig. 5. Particles of magnetic dust from the Sikhote-Alin meteorite shower extracted from the ground magnetically. They are magnetic, porous globules. ×160.

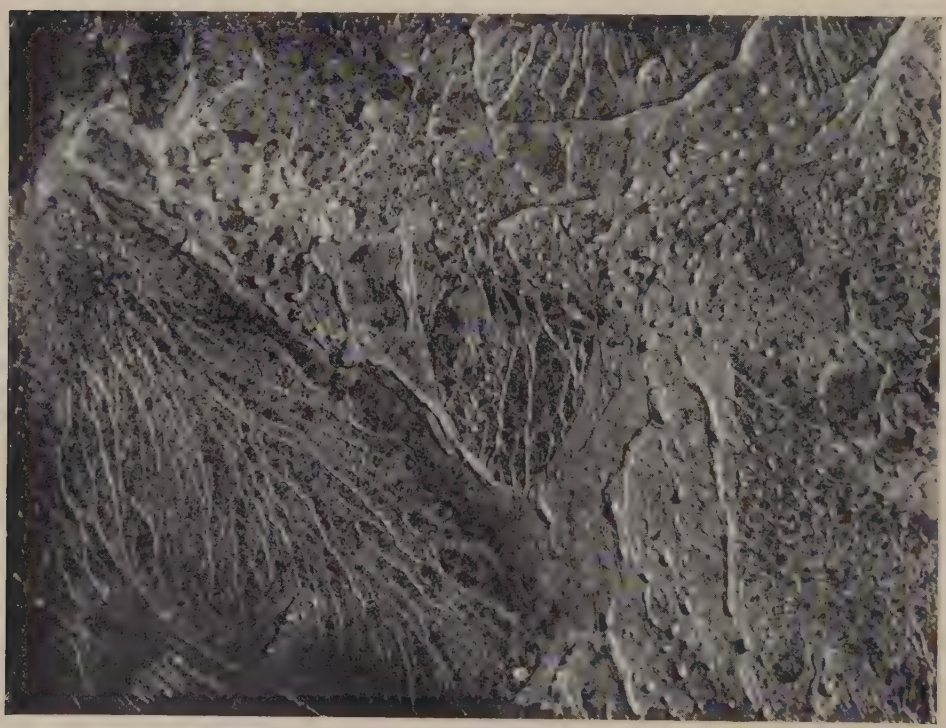

Fig. 6. Complex structure of the melted surface of one of the individual samples of the Sikhote-Alin meteorite shower. ×27.

refers to particles of this range. The Canadian value may be unrealistically low, for it was necessary, because of weather conditions in the Arctic, to use some slides possibly affected by the intermittent formation of frost and ice during exposure.

Summing up, it may be stated that the properties of spherules under discussion, sampled at three widely separated sites, are distinctly alike, not just descriptively, but also as far as quantitative study could be carried. Several attempts were made to carry out microchemical tests for iron and nickel on individual spherules. Their mass, however, proved too small to produce discernible colorimetric reactions.

Discussion

There are at least three conceivable explanations for the origin of these spherules; (a) they might be terrestrial dust, (b) they might be particles arrived from outside the earth's atmosphere essentially intact (the micrometeorites of Whipple, 1950, 1951) or (c) they might, though of extraterrestrial origin, rather be secondary products, namely material lost from larger objects in flight through the earth's atmosphere.

If the first alternative, that the particles are terrestrial, is correct, then it would seem necessary to assume either that they are formed in uniform amounts over a good part of the surface of the earth or that, though of strictly localized origin, they are distributed uniformly over the earth by meteorological transport. It does not seem profitable at this time to speculate on a mechanism for the first of these assumptions; how such spherules could originate in the Arctic is somewhat difficult to conceive.

If the spherules are industrial by-products, we must assume that winds are capable of carrying such particles to high latitudes and of distributing them fairly uniformly over the globe. Certainly under exceptional conditions long distance transportation of small particles does take place. The effects of the 1883 Krakatoa explosion are an outstanding example. More recently Schaefer (1956) and others have obtained evidence of dust having been carried 2000–3000 miles before being deposited.

However, these observations hardly establish that world-wide dispersion of particles, causing a uniform fall-out over the earth, occurs regularly.

The second alternative, that the spherules are micrometeorites (which have not suffered change in passing through the earth's atmosphere) is also difficult to discuss. On this assumption, it would remain to be explained why dust in interplanetary space should be spherical in shape. Any such explanation would have to consist of rather persuasive arguments.

The third possibility, that the spherules are formed from material lost from larger objects in flight through the atmosphere, seems more promising. Krinov and Fonton's investigation (Krinov and Fonton, 1955, Krinov, 1956) of the well-observed Sikhote-Alin meteorite fall, which occurred in Siberia in 1947, have presented incontrovertible evidence that spherules ranging in size from 3 to 100 μ were formed during the meteorite's fall. Soil from the region of dispersion of meteorite particles, which was an ellipse of 2·4 km^2 area, contains not only small angular splinters of iron, ascribed by the authors to fragmentation of the meteorite, but also numerous shiny magnetic spherules: see Figs. 4 and 5.* Moreover, Krinov

found similar particles, along with hollow spheres and tear-drop-shaped objects, scattered along lines of flow on the faces of the larger meteoritic bodies: see Fig. 6.* Chemical analysis revealed that magnetite was the principal constituent of the spherules. They were found to have a porous structure, and were quite fragile.

Spherules claimed to be of extraterrestrial origin have been turned up in a recent study of the dust from cores up to 93 ft deep in the Arctic ice island designated as T-3 (Stoiber, Lyons, Elberty and McCrehand, 1956). Magnetic spherules, some with striated surfaces, some pitted, and some hollow, were discovered throughout the cores. Although the publication does not specify the size of these particles, it may be surmised from their photographs that the larger ones are about 15 μ in diameter. On the basis of microchemical and other tests, it was concluded that the spherules contained magnetite. In the opinion of the authors the more occurrence so deep within the ice precludes any industrial origin of such particles, and a volcanic origin is counter-indicated by their shape and surface markings.

The occurrence of metallic spherules in deep sea sediments, though known for a long time, has but recently attracted more general attention. It is unnecessary to review this problem because a comprehensive discussion has just been given by Öpik (1956). The deep sea spherules are widely believed to be of meteoritic nature but really convincing evidence has been lacking. It would now appear that such doubts have been settled by the work of Smales, Mapper and Wood (1957). A special method of neutron activation analysis developed by these authors has been used to determine trace quantities of cobalt, nickel and copper in spherules isolated from deep sea cores. The quantity of iron present was determined by a colorimetric method. From the nickel/copper, nickel/cobalt, copper/cobalt and nickel/iron ratios they have shown that the deep sea spherules closely resemble iron meteorites. It is doubtless of the greatest importance to have identified in fossil terrestrial material spherules that are indistinguishable by composition from iron meteorites. Unless the sensitivity of the analytic methods employed by the British authors can be much improved, however, it is difficult to see how they could be of use in studying the much smaller spherules of our samples.

Conclusion

Accepting as presumably world-wide the rate of fall of particles and their size distribution described above, the computed accretion for the entire Earth is about 5×10^8 kg/year; this figure assumes a density for the spherules of about 4 g/cm^3 (magnetite) and refers to particles between 3–15 μ in diameter. Recently Whipple (1957) has calculated from Millman's bright meteor data that about 2×10^3 tons of meteoritic material falls to the earth daily. This figure corresponds to 7×10^8 kg/year.

Although the probability that spherical particles like those studied in the present investigation are derived from meteorites is very great, one is not able, because of possible contamination, to state definitely that every spherule is extraterrestrial in origin. It is obviously desirable to obtain such relatively uncontaminated samples

* These photographs were obtained by Prof. Krinov and by his kind permission are included here for the convenience of the reader. Other photographs of dust and spray from the Sikhote-Alin meteorite fall are reproduced in *Principles of Meteoritics* (Krinov, 1955).

of dust as might be collected from high-flying planes or balloons in the Arctic. Preparations for such collections to be made by the Smithsonian Astrophysical Observatory are now in progress.

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During the formulation of our programme we have benefitted from the advice of several scientists interested in related problems, especially Dr. V. J. Schaefer, Dr. W. D. Crozier and Dr. J. F. Heard.

Professor G. E. Hutchinson and Dr. P. Wangersky, of Yale University, have kindly given advice and help with the microchemical tests mentioned above. Mrs. Margot Bergmann, of the Department of Crystallography of the Polytechnic Institute of Brooklyn, has devoted much thought and time to the problem of X-ray analysis of individual spherules isolated from our samples. The difficulties encountered in this early work have not yet been overcome, but her efforts are being continued under the auspices of the Smithsonian Astrophysical Observatory.

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On a correlation between the common lead model age and the trace-element content of galenas

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Abstract—It is now well known that the isotopic composition of common lead varies in a significant way with the age of the lead occurrence. Providing certain assumptions are made, this isotopic composition can be used for an estimate of the age of the mineral. This "model" or "conventional" age is often in accordance with other evidence. However there exist a certain number of leads which do not conform to the systematic pattern generally observed.

The purpose of this study is to investigate certain aspects of the geology and geochemistry of those leads, the model ages of which are older than the geological age. Their isotopic composition usually appears to be perfectly normal and if the age of the host formation or of the emplacement of the lead occurrence is unknown it may be impossible to detect which leads belong to this type, so that the search for criteria enabling to recognize them is of some importance.

Twenty leads from the Alps and twenty-four from North Africa have been studied. In each case the model age, derived from the isotopic composition, has been compared to the age of the host formation or that of the emplacement of the galena. The silver content (and that of some trace elements) of each of these galenas has been measured and compared to the abovementioned ages.

Practically all galenas we have investigated that have model ages comparable to the age of the host formation are found in veins, often with more or less obvious magmatic connexions and they are silver rich. On the other hand the leads of those occurrences, located in sedimentary rocks, and apparently independent of igneous activity, are poor in silver and have model ages which are older than the host formation.

The origin of the latter, "telethermal", type of occurrence has often been debated and it has been suggested that these occurrences are "rejuvenated" from an older source of ore. This seems to be borne out by the fact that it is precisely occurrences of this type which contain leads with model ages older than the age of the host formation.

It thus seems that when the age of the host formation is known, isotope analyses of lead minerals and the model age derived therefrom, constitute objective criteria enabling us to distinguish which occurrences are emplaced for the first time and which are derived or rejuvenated.

In formations of unknown age, a similar criterion which might furnish the same information appears to be the silver content of the galena. In each of the areas studied, we have found that, as regards silver content, there is a sharp distinction, with little or no overlap, between leads with model ages in agreement with the age of the host formation and those with model ages older than that of the host formation.

1. Introduction

It is by now a well established fact that the isotopic composition of common lead varies with the age of the deposit in a significant way. Thus on the basis of certain assumptions these figures can be used for an estimate of the age of lead minerals and it has been shown repeatedly that ages obtained in this way are often satisfactory (Houtermans, 1953; Allan *et al.*, 1953; Russell *et al.*, 1954; Geiss, 1954; Eberhardt *et al.*, 1955; Holmes and Cahen, 1955). It is, however, equally well known that there exist certain common lead deposits in which the isotopic compositions do not fit into the systematic pattern generally observed and which are therefore to be regarded as anomalous. This phenomena is quite independent

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of the particular scheme of calculating ages and thus indicates that the history of the lead of these samples did not follow the general pattern.

The model we have previously chosen (Houtermans, 1953; Geiss, 1954; Eberhardt *et al.*, 1955, 1956; Besairie *et al.*, 1956; Choubert *et al.*, 1956) for the calculation of ages from the isotopic composition of common lead consists in the application of the lead-lead method to common lead. The radiogenic fraction of the isotopes 206 and 207 is computed by subtracting the amounts of primeval lead determined by the Pb^{204} content of the sample. Thus the following equation is obtained:

$$\frac{\beta - \beta_w}{\alpha - \alpha_w} = \varepsilon \cdot \frac{e^{\lambda w} - e^{\lambda' p}}{e^{\lambda w} - e^{\lambda p}} \qquad (1)$$

where

$$\alpha = Pb^{206}/Pb^{204}$$

$$\beta = Pb^{207}/Pb^{204}$$

as measured in the sample

α_w, β_w = isotopic ratios of primeval lead,
ε = (U^{235}/U^{238}) at present,
λ,λ' = decay constants of U^{238} and U^{235} respectively.
w = age of the earth crust,
p = "model age" of the particular common lead sample,

For the primeval lead the isotopic composition of the lead from iron meteorites is taken, as measured by Patterson *et al.* (1953). The validity of this procedure has been discussed previously (Houtermans, 1953; Geiss, 1954).

The application of equation (1) for the dating of common lead depends on the following assumptions. At a certain time, which may be called the time of the formation of the crust of the earth, all its lead had the isotopic composition of the "primeval lead" in iron meteorites. From this time onwards the amounts of Pb^{206} and Pb^{207} have been increased owing to the decay of uranium and similarly, the Pb^{208} owing to the decay of the thorium. This has taken place in a state where the lead is still mixed with the undifferentiated material of the crust; thus the radiogenic lead is added to the primeval lead producing, with time, a change in the isotopic composition. At the time of the formation of a common lead mineral, the lead is separated from the uranium (and thorium) and its isotopic composition has remained constant until the present time. It may be emphasized that the application of equation (1) implies that the ratio uranium/lead in the undifferentiated material has not changed with time except for those changes produced by the decay of the uranium isotopes. The model, however, does not imply a constant U/Pb ratio at the present time in the lead ore-forming parent material through the world.

Of about 150 African lead samples mainly from the Pre-Cambrian, 65–70 per cent seem to be normal, e.g. their model age is in agreement with the age of the host formation or with the age of emplacement as determined by other methods. This agreement is found in the whole range of ages between ca. 50 million years

and 3300 million years (Holmes and Cahen, 1957). A satisfying picture is also obtained for European samples. The remaining 30–35 per cent of the African samples are certainly or possibly anomalous. Two types of anomalies have been distinguished in previous papers (Houtermans, 1953, Geiss, 1954; Eberhardt *et al.*, 1955, 1956).

(1) The first type of anomaly produces model ages that are too young. (This should not be confused with the frequent case of young veins, with normal lead, traversing ancient rocks.) This J-type (from Joplin) anomaly can, in most cases, be recognized by one or more of the following criteria:

(a) Negative ages.

(b) Discrepancies between the Pb^{206}/Pb^{204} and Pb^{207}/Pb^{204} ratios on one hand and the Pb^{208}/Pb^{204} on the other.

(c) Large dispersion of isotopic ratios of lead in material from a single occurrence or from an area where widespread mineralization has occurred contemporaneously.

The history of these J-types must have been different and more complicated than that assumed for the model, one explanation being the addition of radiogenic lead either from uranium or from thorium, or from both, under conditions differing from those implied in the model.

(2) The B-type (from Bleiberg) has been defined as giving a model age greater than the geological age. Whereas the isotopic constitution of the J-type leads is in itself an indication of their anomaly, this is generally not the case with B-types which, judging by their isotopic composition, usually appear perfectly normal. The discrepancy between the model age and the geological age may be entirely due to a geological phenomena, e.g. migration of lead from a normal occurrence to another geological environment (Eberhardt *et al.*, 1955, 1956; Holmes and Cahen, 1955, 1957). The model age of such a B-type would give time of separation of the lead from uranium and thorium. If, after this, the lead is dissolved in a solution which contains neither other common lead nor radiogenic lead it can be transported to another emplacement without any change of isotopic composition. The purpose of the present paper is to study certain aspects of the geology and the geochemistry of these B-type lead ores.

2. Measurement of the Isotopic Composition of Lead

The mass spectrometric measurements were carried out with a 20 cm single-focusing analyser. The material, PbS, was evaporated from a crucible, and the ions were formed by electron impact. The ion current was measured electrometrically by means of a vibrating reed amplifier and a high-precision galvanometer. In all samples the isotopic composition of the lead was determined from the Pb^+ ion beam as well as from the PbS^+ beam. Within the limits of error the results of both agreed in all cases. Details of the measuring procedure have been published previously (Geiss, 1954; Eberhardt *et al.*, 1955; Ehrenberg *et al.*, 1955).

The results are shown in Table 1; the following terms are used: $\alpha = Pb^{206}/Pb^{204}$, $\beta = Pb^{207}/Pb^{204}$, $\gamma = Pb^{208}/Pb^{204}$, p = model age of the common lead sample, $\mu = (U^{238}/Pb^{204})$ at present, and $\kappa = (Th^{232}/U^{238})$ at present; these are the values in the undifferentiated material from which the common lead samples have been

Table 1. Isotopic ratios of lead and model ages

No.	No. of isotope analysis	Locality	α	β	γ	p (million yr.)	μ	κ
1	2	3	4	5	6	7	8	9
1	Be. 48	Les Trappistes, near Martigny (Switz.)	19·23	15·84	39·48	−150 ± 50	9·65	4·15
2	Be. 50	Val d'Anzasca, near Domodossola (Italy)	18·90	15·71	38·94	80 ± 50	9·43	4·08
3	Be. 49	Val d'Antrona, near Domodossola (Italy)	18·98	15·81	39·13	0 ± 60	9·62	4·14
4	Be. 13	Baia Sprie (Felsöbanya) Carpathians (Rumania)	19·03	15·85	39·37	10 ± 40	9·68	4·22
5	Be. 15	Herja, near Baia Sprie, Carpathians (Rumania)	19·05	15·90	39·49	50 ± 50	9·78	4·26
6	Be. 28	Cocorier Mine, near Martigny (Switz.)	18·85	15·75	38·93	20 ± 40	9·51	4·11
7	Be. 45	Cocorier Mine, near Martigny (Switz.)	18·83	15·74	38·93	20 ± 20	9·49	4·12
8	Be. 46	Cocorier Mine, near Martigny (Switz.)	18·87	15·79	39·13	50 ± 30	9·58	4·19
9	Be. 44	Traversella, Piemont (Italy)	18·71	15·69	38·93	40 ± 30	9·41	4·18
10	Be. 47	Dahlstollen, near Goppenstien (Switz.)	18·62	15·77	38·85	210 ± 60	9·57	4·22
11	Be. 43	Wylergraben, near Goppenstein (Switz.)	18·60	15·78	38·77	240 ± 60	9·59	4·20
12	Be. 109	Grimsel Area (Switz.)	18·64	15·82	38·83	250 ± 50	9·66	4·21
13	Be. 52	Praz Jean, Val d'Hérens (Switz.)	18·52	15·76	38·87	270 ± 30	9·56	4·28
14	Be. 111	Taspin Alp, Graubünden (Switz.)	18·55	15·78	38·87	270 ± 50	9·59	4·27
15	Be. 51	Albrun Pass, Binntal (Switz.)	18·55	15·79	38·89	280 ± 50	9·61	4·28
16	Be. 1	Bleiberg, Rolf Shaft (Austria)	18·50	15·80	38·82	330 ± 60	9·64	4·28
17	Be. 2	Bleiberg, Rudolf Shaft (a) (Austria)	18·54	15·84	39·02	350 ± 50	9·71	4·35
18	Be. 10	Bleiberg, Rudolf Shaft (b) (Austria)	18·50	15·82	38·85	350 ± 40	9·67	4·30
19	Be. 11	Bleiberg, Antoni Shaft (Austria)	18·54	15·85	39·00	360 ± 40	9·73	4·35
20	Be. 29	Raibl (Italy)	18·47	15·75	38·77	300 ± 70	9·54	4·27
21	Be. 79	Sidi Amor (Tunisia)	18·85	15·78	39·17	50 ± 60	9·56	4·23
22	Be. 27	Djebel Gustar (E. Algeria)	18·92	15·85	39·17	90 ± 40	9·69	4·20
23	Be. 128	El Mistoui, near Rhafsai, Rif. (Morocco)	18·69	15·76	39·07	140 ± 60	9·54	4·27
24	Be. 78	Sidi Hiah, near Ait Chekrane, Rif. (Morocco)	18·67	15·81	39·25	220 ± 50	9·64	4·37
25	Be. 87	Jorf Ouazzen, S.E. Oujda (Morocco)	18·54	15·77	38·96	280 ± 60	9·57	4·31
26	Be. 127	Tizi n'Recass, Middle Atlas (Morocco)	18·32	15·66	38·63	290 ± 40	9·39	4·28
27	Be. 81	Ait Abbes, Jebel Tizzal (Morocco)	18·48	15·77	38·95	310 ± 60	9·57	4·34
28	Be. 107	Jebel Melias, S.W. Figuig (W. Algeria)	18·47	15·77	38·99	320 ± 50	9·57	4·31
29	Be. 82	Touissit, near Bou Beker (Morocco)	18·55	15·83	39·16	330 ± 50	9·69	4·07
30	Be. 84	Imilchil, S.W. Tirrhist (Morocco)	18·55	15·83	39·15	330 ± 30	9·69	4·40
31	Be. 41	Mibladen (H. Moulouya) Bou Tazzoult (Morocco)	18·30	15·67	38·65	320 ± 40	9·41	4·30
32	Be. 26	Mibladen (H. Moulouya) Bou Selloum (Morocco)	18·35	15·74	38·72	370 ± 50	9·54	4·32
33	Be. 40	Mibladen (H. Moulouya) Quarry (Morocco)	18·37	15·81	38·80	430 ± 60	9·67	4·36
34	Be. 149	Aouli (H. Moulouya) Henri (Morocco)	18·21	15·66	38·62	370 ± 60	9·40	4·34
35	Be. 148	Aouli (H. Moulouya) Henri niv. O (Morocco)	18·26	15·72	38·70	420 ± 60	9·50	4·36
36	Be. 39	Aouli (H. Moulouya) Bou Adil (Morocco)	18·25	15·73	38·61	420 ± 60	9·53	4·32
37	Be. 108	Sidi Lahcen, Karrouba, S.W. Tedders (Morocco)	18·57	15·80	39·11	290 ± 50	9·63	4·36
38	Be. 125	Tamjout, near Taroudant (Morocco)	18·30	15·71	38·04	370 ± 40	9·48	4·03
39	Be. 80	Kerkour, Jebilet (Morocco)	18·33	15·76	38·50	400 ± 60	9·57	4·23
40	Be. 126	MFis, near Taouz (Morocco)	18·26	15·72	38·58	410 ± 40	9·51	4·30
41	Be. 147	Jebel Khetem, (central Morocco)	18·37	15·80	38·83	420 ± 70	9·65	4·36
42	Be. 83	Erdouz, S. W. Amizmiz (Morocco)	18·23	15·73	38·43	440 ± 40	9·72	4·26
43	Be. 85	Tabouchent, near Marrakech (Morocco)	18·52	15·94	39·44	470 ± 70	9·90	4·57
44	Be. 86	Gundafa, H. Atlas near Marrakech (Morocco)	17·96	15·63	37·82	520 ± 70	9·38	4·12

derived, as calculated from the isotopic composition of the lead. The errors given for the model ages represent the errors of the isotopic measurements.

3. Spectrochemical Analysis of Silver in Galena

Spectrochemical analyses of trace elements in galenas have been carried out by numerous workers. A recent survey by Fleischer (1955) gives a list of publications on this topic and brief indications on the conclusions reached in the fields of geochemistry, paragenesis, cristallochemistry and mineralogy.

The particular object of the present work was to detect trace elements in galenas of known stratigraphical environment and lead isotope constitution in order to compare both "geological" age and "isotopic" age with trace element content.

Choice of analytical method

Among the numerous spectrochemical methods we have chosen one suited to the following requirements:

(1) Simultaneous search for numerous elements present in extremely varying concentrations. (2) Possibility of analysing only small quantities (5–10 mg) because of lack of more material in some cases. (3) Quick and simple method of preparing numerous samples.

As regards excitation conditions we chose the method of Mannkopff and Peters (Mitchell, 1948) and as regards measurement of line intensity, that of Harvey (1947), in which the intensity of the background is taken as internal standard.

Analytical procedures and conditions

Galena specimens were prepared by crushing clean fragments to minus 200 mesh and mixing them with an equal weight of carbon. A series of standard mixtures containing the following elements, were prepared according to the method described by Mitchell (1948): Sn, Sb, Ag, Cd, As, Mn, Ga, Ge, Zn, Cu, Mo, Tl, Bi. The concentration of each element ranged from 1 to 0·001 for one hundred parts of chemically precipitated PbS.

Apparatus. Hilger spectrograph E. 492. Rotating 6-step-sector. Lower part of collimating lens masked. Reading of spectrograms and photometry with Fuess magnifying-microphotometer 11852. Excitation conditions: lower electrode (cathode) carrying the specimen, 2 min exposure at 220 V (d.c.) and 9 A/hr. Gap between electrodes: 10 mm.

Results

In the case of elements other than silver, measurements made on galenas of very different ages and stratigraphical environment, from Morocco and central Africa, failed to show any obvious relation between presence or concentration of trace elements and other genetic peculiarities (age, stratigraphical situation, paragenesis, metallogenetic province). The silver content, on the other hand, bears a relationship to these factors. It was therefore decided to place more emphasis on the detection and analysis of this element.

Precision of the measurements

In the majority of cases, measurements are reasonably reproducible and the

average deviation of a single measurement (for three measurements performed at the same time) is 25 per cent. In the same way, repeated measurements on galenas freshly separated, crushed, and mixed with carbon, show a deviation of the same order. In some cases it has been very difficult to obtain coherent figures for certain galenas, specially in the case of galena-carbon mixtures which were prepared several months before the spectrograms were taken. Such irregularities are probably due to the heterogeneous silver distribution in certain galenas and to mechanical separation due to vibrations. In these cases a large number of measurements have been performed in order to obtain a reasonable average.

With this method the lower limit of sensitivity is rather high (0·03–0·01 per cent). This is due to the fact that the method proposed by Harvey implies the existence of a measurable background whose intensity may be compared to that of the line. Below 0·01 per cent, the intensities of the silver line and of the background are comparable with the instrumental errors.

4. Discussion of Data

In the following pages we have compared the model age of the leads of the age of the host formation or to the age of emplacement of the ore. When possible, preference has been given to the age of the host formation which is less liable to interpretation.

When the age of the host formation equals the model age of the lead, taking into account the indicated limits of error, we say that the model age agrees with that of the host formation. There is no disagreement if the model age is younger than the age of the host formation, into which the ores may be intruded (except possibly in the case of J-type anomalous leads).

We say that the model age disagrees with the age of the host formation when it is greater than the latter.

It is obvious that for young ages (for example 50 ± 50 million years), if the age of the host formation is 10 million years, the agreement does not exclude the possibility that the lead is, in fact, a mixture of young lead approximately 10 million years in age with older lead. However, in both of the investigated areas the older leads are at least Hercynian in age and it is hence obvious that in cases like the example, the quantity of older lead that eventually may be admixed is very small.

(*a*) *Alpine Leads*

We have investigated twenty lead samples. Eighteen of these come from the Alps (Switzerland, Italy and Austria) and two came from the Carpathians (Rumania). Two of these leads are certainly J-type anomalies (Nos. 1 and 2). A certain number of leads with young model ages are to be considered as doubtful, possibly belonging to the same anomalous type since there is a marked disagreement between the model age and the 208/204 ratio (Nos. 6, 7 and 9). By analogy, No. 8, from the same mine as Nos. 6 and 7, and No. 3, from the immediate neighbourhood of No. 2 are also doubtful, though the isotopic analysis reveals no important disagreement between the 208/204 ratio and the model age.

None of the Swiss or Italian leads with young model ages can with certainty

Table 2. Leads from the Alpine region

No.	No. of isotope analysis	Locality	Model ages (million yr)	Youngest host formation (with age (million yr), after Holmes, 1947)	Age of emplacement million yr	Reference for geolog. data	Silver content (p.p.m.)
1	Be. 48	Les Trappistes, near Martigny (Switz.)	-150 ± 50	Crystalline schists of Mt. Blanc massif pre-Triassic, >180	Alpine (<50)	1, 2, 3	725
2	Be. 50	Val d'Anzasca, near Domodossola (Italy)	-80 ± 50	Gneiss and micaschists, probably pre-Triassic, >180	Alpine (<50)	4, 3	1175
3	Be. 49	Val d'Antrona, near Domodossola (Italy)	0 ± 60	Granitic gneiss, probably pre-Triassic, >180	Alpine (<50)	4, 3	1500
4	Be. 13	Baia Sprie (Felsöbanya) Carpathians (Rumania)	10 ± 50	Lower Pliocene, ca. 10	Pliocene (ca. 10)	5, 6	2275
5	Be. 15	Herja, near Baia Sprie, Carpathians (Rumania)	50 ± 50	Lower Pliocene, ca. 10	Pliocene (ca. 10)	5, 6	>1000 (6)
6	Be. 28	Cocorier Mine, near Martigny (Switz.)	20 ± 40	Paragneisses of the Aiguilles rouges massif; pre-Triassic, >180	Hercynian or younger (≤240)	1, 2, 3	400
7	Be. 45	Cocorier mine, near Martigny (Switz.)	20 ± 40	Paragneisses of the Aiguilles rouges massif; pre-Triassic, >180	Hercynian or younger (≤240)	1, 2, 3	450
8	Be. 46	Cocorier Mine, near Martigny (Switz.)	50 ± 30	Paragneisses of the Aiguilles rouges massif; pre-Triassic, >180	Hercynian or younger (≤240)	1, 2, 3	400
9	Be. 44	Traversella, Piemont (Italy)	40 ± 30	Dolomitic limestone, probably pre-Triassic, >180	Hercynian or younger (≤240)	3	1200
10	Be. 47	Dahlstollen, near Goppenstein (Switz.)	210 ± 60	Cristalline schist of Aare massif pre-Triassic, >180	Hercynian ≈240	7, 3	780
11	Be. 43	Wylergraben, near Goppenstein (Switz.)	240 ± 60	Cristalline schist of Aare massif pre-Triassic, >180	Hercynian ≈240	7, 3	300
12	Be. 109	Grimsel Area (Switz.)	250 ± 50	Grimsel granite, Aare massif pre-Triassic, >180	Hercynian ≈240	3	320
13	Be. 52	Praz Jean, Val d'Hérens (Switz.)	270 ± 30	Gneiss, pre-Triassic, >180	Hercynian ≈240	7, 3	1600
14	Be. 111	Taspin Alp. Graubünden (Switz.)	270 ± 50	Gneiss, pre-Triassic, >180	Hercynian or younger (≤240)	8	2700
15	Be. 51	Albrun Pass, Binntal (Switz.)	280 ± 50	Dolomite, probably pre-Triassic, >180	?	3	1600
16	Be. 1	Bleiberg, Rolf Shaft (Austria)	330 ± 60	Carnian (Upper Trias.), ca. 160	Triassic or younger (≤160)	9, 10	<100(10)
17	Be. 2	Bleiberg, Rudolf Shaft (a) (Austria)	350 ± 50	Carnian (Upper Trias.), ca. 160	Triassic or younger (≤160)	9, 10	<100
18	Be. 10	Bleiberg, Rudolf Shaft (b) (Austria)	350 ± 40	Carnian (Upper Trias.), ca. 160	Triassic or younger (≤160)	9, 10	<100
19	Be. 11	Bleiberg, Antoni Shaft (Austria)	360 ± 40	Carnian (Upper Trias.), ca. 160	Triassic or younger (≤160)	9, 10	<100
20	Be. 29	Raibl (Italy)	300 ± 70	Carnian (Upper Trias.), ca. 160	Triassic or younger (≤160)	9, 10	<100

(1) Ladame (1935)
(2) Rickenbach and Kaenel (1953)
(3) Huegi (1957)
(4) Huttenlocher (1954)
(5) Ghitulescu (1935)
(6) Gesell (1893)
(7) Huttenlocher (1931)
(8) Escher (1935)
(9) Holler (1953)
(10) Schroll (1953)

be considered as normal leads of Alpine age: however the two Carpathian specimens appear quite normal and in agreement with their geological environment.

The results of our investigation are shown in Table 2 and Fig. 1. The four Bleiberg specimens (Nos. 16 to 19) yield remarkably constant model ages which are distinctly greater than the Triassic host formations. The silver content of these ores is extremely low, less than 1 g/ton according to industrial analyses (Schroll, 1953) (or less than 100 p.p.m. which is the lower limit of detection by spectrochemical analysis).*

The specimen from Raibl, (No. 20) about 15 km south of Bleiberg and located in the same Triassic host formation, also displays a model age which is distinctly greater than the age of the host formation. The silver content is also extremely low in analogy with the Bleiberg specimens.

All specimens from Switzerland which are, or could be, of Hercynian age (Ladame, 1935; Rickenbach and von Känel, 1953; Huttenlocher, 1934, 1954; Hügi, 1957) have model ages in agreement with this age and a silver content greater than 300 p.p.m.

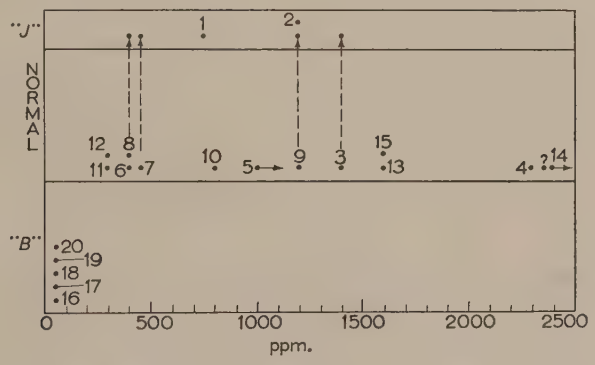

Fig. 1. Leads from Alpine region Silver content (p.p.m.) of normal B-type and J-type leads.

The specimens with Alpine model ages, and which are, or could have been, emplaced during Tertiary times (Ladame, 1935; Rickenbach and von Känel, 1953; Huttenlocher, 1954; Hügi, 1957; Ghitulescu, 1935; Gesell, 1893), irrespective of whether they are normal leads, doubtful or J-type leads, all have a silver content of over 400 p.p.m.

There is therefore a sharp distinction between the silver content of those specimens with model age older than host formation, B-type leads, on the one hand, and that of specimens with "normal" lead on the other hand. J-types, certain or presumed, are in this case, like the latter in respect of silver content.

(*b*) *North African Leads*

Of twenty-four North African leads so far analysed only three show any sign of being J-type anomalous leads. These are Nos. 38, 43 and 44, which show a rather marked disagreement between their model ages and the value of the 208/204 ratio. The first and third cases appear to correspond to a lead which is older than

* Throughout this paper, industrial chemical analyses are expressed as g/ton, spectrochemical analyses as p.p.m.

Table 3. Leads from North Africa

No.	No. of isotope analysis	Locality	Model Ages (million yr)	Youngest host formation (With age (million yr) after Holmes, 1947)	Reference for geolog. data	Silver content		Ref. for Ag cont. (gr/ton)
						chemical (gr/ton)	spectroch. (p.p.m.)	
21	Be. 79	Sidi Amor (Tunisia)	50 ± 60	Lower Cretaceous, ca. 90–127	1	400	1450	1
22	Be. 27	Djebel Gustar (E. Algeria)	90 ± 40	Lower Cretaceous, ca. 90–127	2	≈900	800	2
23	Be. 128	El Mistoui, near Rhafsai, Rif. (Morocco)	140 ± 40	Upper Cretaceous, ca. 58–90	3, 4	100	<100	3
24	Be. 78	Sidi Hiah, near Ait Chekrane, Rif. (Morocco)	220 ± 50	Jurassic-Cretaceous flysch, ca. 127	4	—	300	
25	Be. 87	Jorf Ouazzen, S.E. Oujda (Morrocco)	280 ± 60	Toarcian–Bajocian, 127–152	5, 6	130	—	6
26	Be. 127	Tizi n'Recass, Middle Atlas (Morocco)	290 ± 40	Middle Lias, 127–152	7	—	<100	
27	Be. 81	Ait Abbes, Jebel Tizzal (Morocco)	310 ± 60	Domerian, 127–152	3, 7	—	<300	
28	Be. 107	Jebel Melias, S.W. Figuig (W. Algeria)	320 ± 50	Dogger, 127–152	3	150	—	6
29	Be. 82	Touissit, near Bou Beker (Morocco)	330 ± 50	Toarcian–Bajocian, 127–152	3	250–420	—	6
30	Be. 84	Imilchil, S.W. Tirrhist (Morocco)	330 ± 50	Upper Lias, 127–152	6	—	400	
31	Be. 41	Mibladen (H. Moulouya) Bou Tazzoult (Morocco)	320 ± 40	Lias, 127–152	3, 8		420	
32	Be. 26	Mibladen (H. Moulouya) Bou Selloum (Morocco)	370 ± 50	Lias, 127–152	3, 8	220–270	360	5
33	Be. 40	Mibladen (H. Moulouya) Quarry (Morocco)	430 ± 60	Lias, 127–152	3, 8		<300	
34	Be. 149	Aouli (H. Moulouya) Henri (Morocco)	370 ± 60	Permo-Triassic conglomerates, ~180	3, 8	400–450	1250	
35	Be. 148	Aouli (H. Moulouya) Henri niv. O (Morocco)	420 ± 60	Permo-Triassic conglomerates, ~180	3, 8	more at	880	5
36	Be. 39	Aouli (H. Moulouya) Bou Adil (Morocco)	420 ± 60	Permo-Triassic conglomerates, ~180	3, 8	depth	1725	
37	Be. 108	Sidi Lahcen, Karrouba, S.W. Tedders (Morocco)	290 ± 50	Visean, ca. 245	3, 8	800	—	
38	Be. 125	Tamjout, near Taroudant (Morocco)	370 ± 40	Infrageorgian, >520	10, 7	450	630	10
39	Be. 80	Kerkour, Jebilet (Morocco)	400 ± 60	?Visean, ca. 245	9	100	400	6
40	Be. 126	MFis, near Taouz (Morocco)	410 ± 60	Visean, ca. 245	3	350	500	5
41	Be. 147	Jebel Khetem, central Morocco	420 ± 70	Ordovician, 350–430	7	—	1380	
42	Be. 83	Erdouz, S.W. Amizmiz (Morocco)	440 ± 40	Georgian, ca. 480–520	3, 9	1500–2600	—	6
43	Be. 85	Tabouchent, near Marrakech (Morocco)	470 ± 70	post Visean granite, <245	9	100	—	6
44	Be. 86	Gundafa, H. Atlas near Marrakech (Morocco)	520 ± 70	Georgian, ca. 480–520	3	350	>1200	3,6

(1) Gottis and Sainfeld (1952)
(2) C.M.D.G. (1956)
(3) Bouladon (1952)
(4) Agard (1956)
(5) Bouladon (1956a)
(6) Choubert (1956)
(7) B.R.P.M. (1955)
(8) Bouladon (1956)
(9) Choubert *et al.* (1956)
(10) Chazan (1954)

the model age (e.g. a Pre-Cambrian lead) and in the second case to a lead which is much younger than the model age. Interpretation of these three occurrences is therefore rather doubtful.

Table 3 shows that, of eight galena leads emplaced in Palaeozoic beds, four have model ages which, within the indicated precision range, are in agreement with their geological situation. These are Nos. 37, 41, 42 and 44; No. 44 is, however to be regarded as a possibly anomalous lead. Three of the galena leads are older than the host formation (Nos. 39, 40 and 43), the latter being possibly an anomalous lead. One of the galenas (No. 38) is younger than the host formation but also possibly anomalous.

Similarly, of thirteen galena leads emplaced in Mesozoic beds and three leads from veins which cut the Permo-Triassic, only two (Nos. 21 and 22) have model ages in agreement with their geological environment. All others are too old, though not all to the same extent.

At first sight the stratigraphical distribution of these model ages seems chaotic and, with a few exceptions, (Nos 21, 22 and 44, and possibly 23 and 24) all Moroccan leads could be related; their isotope ratios fall in a comparatively narrow range and they could all belong to one mineralization of model age 375 ± 95 million years.

Such an interpretation, however, would not take into account the stratigraphical distribution of the specimens.

Relation between model ages and stratigraphy

The lead-ores examined fall into three groups:

(1) *Ores located in Cretaceous rocks.* (Nos. 21 to 24). The model ages of these four minerals range from 50 ± 60 to 220 ± 50 million years. The average model age is 125 million years. Two of these minerals show model ages in agreement with their stratigraphic position, the other two are too old. The time of mineralization is generally considered to be Tertiary.

(2) *Ores located in Jurassic and Permo-Triassic rocks.* Nine galenas are situated in Jurassic rocks and three are in veins which cut Permo-Triassic rocks. The model ages of this group range from 430 ± 60 to 280 ± 60 million years. The majority (nine out of twelve) fall into the more restricted range 370–280 million years. The average age for the whole series is 350 million years. The time of mineralization of these occurrences is generally considered to be Tertiary.

(3) *Ores located in Paleozoic rocks.* Eight galenas (Nos. 37 to 44) are included in this category. The model ages range from 520 ± 70 to 290 ± 50 million years but with one exception they fall into the more restricted range 520–370 million years. The average model age of the whole group is 415 million years. Four of these galena-leads have a model age in agreement with the age of the host rocks, one is younger and three are older. The time of mineralization for these occurrences is often considered to be Hercynian.

Despite the chaotic first impression, there is an obvious relation between model ages and stratigraphy: practically all leads located in Paleozoic beds have model ages greater than those in Jurassic rocks. Latter leads, in turn have model ages greater than those located in Cretaceous formations.

Furthermore, the fact that in the first and third group a certain number of lead ores have model ages which agree with the age of the host formation indicates that at least two periods of mineralization have taken place. One, or perhaps two, in Paleozoic times, and one in post-Cretaceous times.

From the number of leads which fall in the range 400 to 440 one may consider that 420 million years is the approximate age of a "primary" or "juvenile" lead mineralization. One other may have occurred later, at ca. 290 $\pm$ 50 million years and could possibly be Hercynian; a third has occurred in Cretaceous or more probably Tertiary times.

Relation between model age and mode of occurrence

Moroccan (and Western Algerian) lead occurrences have been subdivided into three main groups (Bouladon, 1952): (a) vein occurrences, (b) replacement occurrences and (c) a mixed type, linked with faults and fissures (*gîtes de cassures*). The two latter types of occurrences are mainly found in the post-Triassic beds whereas true veins are more numerous in Paleozoic or Pre-Cambrian beds. The four Moroccan lead ores with model ages in agreement with host formation are to be found in the vein occurrences; so are the two youngest Moroccan occurrences which have model ages older than the host formation and that of Aouli (Nos. 34–36) which may be a rather special case. There is not much difference between the two latter groups of occurrences (*b* and *c*). However in Group (*c*) the model ages are slightly younger than in Group (*b*). In both these groups all leads have model ages distinctly older than that of the host formation.

Of the two Eastern Algerian and Tunisian occurrences, one, Sidi Amor, in Tunisia (No. 21) displays both vein mineralization and replacement, whereas at Djebel Gustar, eastern Algeria (No. 22), only replacement is known. The replacement, however, is linked with faults which have not been explored at depth. In both these eastern occurrences, the lead has a model age in agreement with the age of the host formation and the usually postulated Tertiary age of emplacement lies within the precision range.

Relation between model age and silver content of galena

A comparison of all elements known from the lead ore occurrences (or found by spectrochemical means in the analysed galena specimen) with model ages has led to no definite conclusions except in the case of silver content. This may be in part due to the fact that the known data are not complete in each case.

The relation between model age and silver content (in g/ton or p.p.m.) is apparent in Table 3, and in Fig. 2.

The table shows that of nine cases where spectrochemical analyses can be compared to industrial assays, seven are in reasonably good agreement, whereas in two cases there is a large discrepancy. In the latter cases the figures obtained by spectrochemical means have been checked and have been adopted here as they were obtained on the actual galenas, the leads of which were submitted for isotope analysis. Variability in the silver content of galena in a single mine can notably be explained by recrystallization of portions of the galena, zoning of the mineralization, etc.

If the three possibly J-type anomalous leads (Nos. 38, 43 and 44) are excluded, all leads except three with model ages older than host formation have a low silver content, whereas all leads with model ages in agreement with the age of the host formation have a high silver content. If the three above-mentioned, possibly anomalous, leads are included the only change in the picture is that the two groups become less well separated. The three exceptions (Nos. 34 to 36) are leads from Aouli which may be a rather special case (see below).

The situation can be summarized thus: galenas with leads of model age older than the host formation have a silver content of less than 500 p.p.m., whereas

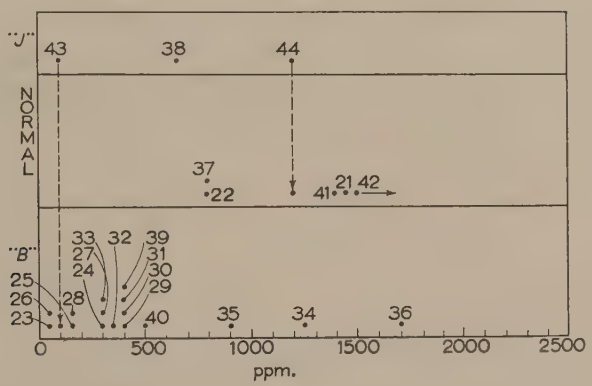

Fig. 2. Leads from North Africa. Silver content (p.p.m.) of normal B-type and J-type leads.

those whose leads have a model age in agreement with the age of the host formation have a silver content of more than 800 p.p.m.; one galena which contains possibly anomalous lead has a silver content of 630 p.p.m.

Aouli-Mibladen area

Six specimens from this area were studied. At Aouli, veins are located in undated, perhaps Palaeozoic, micaschists but sometimes reach Permo-Triassic conglomerates (Bouladon, 1952, 1956). The old Palaeozoic massif is separated from the Mesozoic covering by faults. Along these and parallel faults, especially near Mibladen, the lead ore forms replacement deposits mainly in Liassic limestone and occasionally in Cretaceous beds.

The current opinion on the emplacement of these ores is that the veins of Aouli and the replacement ore-bodies of Mibladen are two phases of the same mineralization and were emplaced in post-Cretaceous times (Bouladon, 1956).

Part of this hypothesis is confirmed by our work: there is no doubt that the ores we have studied from Aouli and from Mibladen are related. However, the general geological environment, together with the model ages found, suggest that the Mibladen ores, located in Mesozoic beds, derive from an earlier mineralization.

It seems that different groups could be recognized among the Aouli veins (Bouladon, 1952): some, in the vicinity of Outat-Sidi Said appear to be distinct from the post-Mesozoic faulting, whereas others, near Aouli proper, appear to be linked to it. The latter are, in fact, post-Premo-Triassic.

The only Aouli ores we have studied come from this latter group and it is noteworthy that among them are to be found the only exceptions to the relationship between silver content and model age, all specimens showing a high silver content. According to Bouladon (1956), the silver content of the Aouli veins is much higher at depth than near the surface, where it is comparable to that of the Mibladen ores.

Two mechanisms seem to be compatible with the available evidence:

(a) All Aouli and Mibladen ores have been emplaced at the same time in post-Cretaceous times (Bouladon, 1956) but are derived from an unknown source approximately 420 million years old.

(b) Some of the Aouli veins, in particular those round Outat-Sida Said, represent the original mineralization of 420 million years. Others, in particular those round Aouli, appear to be connected in some way with the post-Mesozoic faulting. These, which are the ones we have studied, may contain galena in its original condition and galena deposited, like that of Mibladen, after migration.

We hope that circumstances will allow renewed investigations of this interesting mining area.

(c) *Other Leads*

The relationship between the age of emplacement, the model age and the silver content of galenas outlined here seems to hold for galenas from other areas too:

(a) The model ages of certain galena-leads from Africa, South of Sahara, which have been determined previously (Geiss, 1954; Eberhardt *et al.*, 1955, 1956) are presumed to be in agreement with their geological setting. In some cases this can be checked by independent age determinations (Holmes and Cahen, 1957). The silver content, as determined so far, is higher than 1500 p.p.m. in each case.

(b) The isotope constitution of leads of west German galenas has also been investigated (Geiss, 1954) and the silver content of some of the galenas has been measured or checked. The same relation as in the Alps or North Africa is apparent in the limited number of examples so far studied.

5. Summary

Alps

We have examined the relation between model age of lead, silver content of galena and age of emplacement for twenty lead-ores from the Alps and Carpathians.

It is found that, in those cases where the model age is older than the age of the host formation or the presumed age of emplacement, the silver content is low (practically 0 p.p.m.). On the other hand, it is higher (over 300 p.p.m.), and sometimes much higher, in those cases where the model age is in agreement with the geological setting. J-type anomalous ores seem to have a silver content which is not essentially different from that of the latter.

North Africa

For twenty-four lead ores we have studied the relation between model age, stratigraphical situation, mode of occurrence and silver content of galena. Our findings can be expressed as follows:

(1) There is a relation between the silver content of the lead ores, the model ages of the leads and the geological environment of the ores. In cases of agreement between model age and geological setting, the silver content is high (800 p.p.m. and more). On the other hand in those cases where the model age is older than the age of the host formation the silver content is lower (500 p.p.m. and less).

One instance is intermediate between 500 and 800 p.p.m., occurring in a galena with probably J-type anomalous lead. Two other similar anomalous leads occur in galenas with silver content respectively lower than 500 p.p.m. and higher than 800 p.p.m. There are also three exceptions, all located within the same mine.

(2) There is also a relation between mode of occurrence and model age as also between mode of occurrence and silver content. In Morocco all cases of agreement between model age and age of host formation and all ores with high silver content are to be found in vein occurrences. In Morocco again, replacement and mixed occurrences of lead-ores have model ages greater than the age of the host formation. Some vein occurrences are in the same case. In all these cases the silver content is low (less than 500 g/ton).

There is one possible exception in eastern Algeria, at Djebel Gustar which appears to be a mixed occurrence: replacement linked with faults and fissures. Here the model age agrees with age of host formation and there is a high silver content (see p. 142).

The relation between silver content and mode of occurrence seems to be valid for all Moroccan occurrences as Bouladon (1949) has shown that all occurrences with high silver content (over 500 g/ton) are veins, whereas those of lower silver content (less than 500 g/ton) are generally replacement occurrences which may or may not be linked with faults and fissures; however, certain veins also have low silver content.

(3) In those cases where the model age of leads is older than the age of host formation a certain difference is to be noted when one compares the Alpine leads of this type and the Moroccan ones: at Bleiberg and Raibl the model ages of five specimens are very constant, whereas for Mibladen specimens, for instance, they are much more dispersed. This dispersal is greater still if all Moroccan leads located in the Liassic are considered.

6. Conclusions

The theory of the common-lead method implies that leads with model ages older than the host formation are derived from an older mineralization. There is more than one possible mode of derivation, giving rise to epigenetic or syngenetic ore-deposits at a later period.

The facts that have just been summed up show that lead-ores with this type of geologically anomalous model ages do not occur in a random way.

It has generally been agreed that those lead ores with more or less obvious magmatic connexions and silver enrichment are formed at comparatively high temperature and preferentially occur in veins (Dunham, 1948). This type of lead ores has generally been considered as "primary". This is the situation of practically all those lead ores we have studied which have model ages of the right order of magnitude as compared with their host formation.

The origin of lead-zinc ores occurring in sedimentary rocks apparently independently of igneous activity, and formed at low temperature, has been much discussed. These ores are often called "telethermal". It has been suggested that this type of occurrence is "rejuvenated" from an older source of ore (Schneiderhöhn, 1949). The fact that it is precisely occurrences of this type that contain leads with model ages older than the age of the host formation, confirms the main contention of this "rejuvenation" or "migration" hypothesis.

It therefore seems that when the age of the host formation is known, isotope analyses of lead minerals, and the "model" or "conventional" ages derived therefrom, constitute objective criteria enabling us to distinguish which occurrences are emplaced for the first time and which are derived or rejuvenated B-types.

In the case of formation of unknown age, a similar criterion, which in many cases might furnish the same information, appears to be the silver content of the galena, as in each of the areas that have been studied we have found that there is quite a sharp distinction, with little or no overlap between B-types and normal leads, as regards silver content. However, the critical value or interval is not the same in each area.

It would be premature, at this stage, to interpret the difference which has been noted between the Alpine B-type so far investigated, which are extremely poor in silver, and the Moroccan ones which often contain 300–400 p.p.m. of silver. However the following explanations can be considered as working hypotheses:

(a) The Bleiberg and Raibl ores, are rejuvenated without addition of "juvenile" ore whereas the Moroccan leads are mixtures, in varying proportions of migrated and "juvenile" lead.

(b) The Bleiberg ores, though derived from an ancient source are syngenetic ores, eventually reworked, whereas the Moroccan ones are epigenetic ores, migrated and mixed as mentioned above.

The present research mainly contains evidence of statistical order. We are continuing this work by study of interesting occurrences of which the geological history is well known and which, itself, constitutes further evidence of the relation between silver content (and content of other elements) and migration or derivation of lead ores.

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We have been able to discuss these questions with most of the above mentioned persons and also with Prof. E. Niggli and Drs. E. Picciotto and R. D. Russell.

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REPORT OF MEETING

Symposium on Geochemistry, Paris, 22–24 July 1957

The Commission on Geochemistry of the International Union of Pure and Applied Chemistry arranged, on 22–24 July 1957, a Symposium on Geochemistry in Paris. This second Symposium on Geochemistry was organized in conjunction with the meeting of the Commission and with the XVIth International Congress of Pure and Applied Chemistry. Professor Tom F. W. Barth, now President of the Commission on Geochemistry, presided over the Symposium that had been organized, in a most efficient manner, by Professor E. Raguin of the École des Mines at Paris in his capacity of the local Chairman. One hundred and fourteen members, representing a total of twenty countries, attended the Symposium.

The material presented at the Symposium was divided into the following groups: (1) Distribution of elements in the crust of the Earth, (2) cosmochemistry, (3) radioactive elements and geochronology, (4) geochemistry of the lithosphere, (5) geochemistry of the hydrosphere, (6) geochemical prospecting, (7) geochemistry of ores and petroleum, and (8) theoretical geochemistry. Abstracts of the papers presented, some of which have been edited by the authors or by the Secretary of the Commission on Geochemistry, are presented in the following, arranged in alphabetical order.

Kalervo Rankama, Secretary,
Commission on Geochemistry

Trace-element variations across a calcite–dolomite transition in a single thin carbonate bed. John A. S. Adams, Department of Geology, The Rice Institute, Houston, Texas, U.S.A., and Donald R. Lewis, Exploration and Production Research Division, Shell Development Company, Houston, Texas, U.S.A.

Sixty samples from a limestone–dolomite transition in the Ellenburger Ordovician limestone (Blanco County, Texas) have been analysed for major and trace elements by spectrochemical and other techniques. Aluminium, barium, iron, manganese, silicon, sodium, strontium and uranium were found in measurable amounts in nearly all samples. The general level of concentration is within the range of published data, but the dolomites have a higher average trace-element concentration and a greater range of concentrations relative to the calcites. The finer-grained dolomites possess the higher trace-element concentration and higher percentages of noncarbonate material. The lateral variations in trace-element concentration exceed the vertical variations reported in some trace-element correlation studies.

The thermoluminescence properties of these sixty samples were studied. A correlation was found between grain size and absolute peak intensities of the natural thermoluminescence glow curves. The ratios of glow curve peaks after Co^{60} gamma-ray irradiation can be used to determine dolomite–calcite ratios. This method was compared with differential thermal analysis, versenate, and infra-red analysis methods. The infra-red method agrees most closely with the thermoluminescence, and it is concluded that the glow curve peak heights are more related to the gross composition and structural defects than to trace-element concentration.

Localisation des éléments radioactifs dans les sédiments oceaniques récents. G. Arrhenius et N. M. Bramlette, Scripps Institution of Oceanography, La Jolla, California, U.S.A., et E. Picciotto, Service de Physique Nucléaire, Bruxelles, Belgique.

La distribution de la radioactivité alpha a été étudiée dans des carottes de sédiments océaniques récents provenant de la zone nord-équatoriale du Pacifique. On sait que dans les parties superficielles, cette activité est principalement due à l'ionium et ses descendants. Cette étude a été effectuée à l'aide des émulsions nucléaires Ilford C-2. Deux techniques ont été

utilisées: l'autoradiographie de sections congelées des carottes et la mise en suspension du sédiment au sein de l'émulsion. Les résultats obtenus jusqu'à présent sur ces sédiments permettent d'établir les conclusions suivantes:

(a) La distribution originale des éléments radioactifs est perturbée après le dépôt du sédiment par des transports de matériel dus aux organismes vivants.

(b) Les micro-organismes siliceux (diatomées et radiolaires) sont inactifs.

(c) Environ 25% de l'activité alpha est associée à des lamelles brunâtres de quelques dizaines de microns, constituées d'apatite fibreuse et de matière organique et représentant fort probablement des débris de squelettes de poissons. Ces débris sont également enrichis en métaux lourds, tels que terres rares, zinc, cuivre, étain et plomb. L'enrichissement en éléments lourds et radioactifs s'est produit rapidement après le dépôt du sédiment.

Recherche d'indices minéralisés en plomb et zinc par prospection microchimique a grande échelle dans le Détroit Poitevin. C. Beaumont, Bureau de Recherches Géologiques et Géophysiques, Paris, France.

Les études microchimiques de détail, déjà réalisées dans le Détroit Poitevin, ont conduit le B.R.G.G.M. à utiliser les méthodes de prospection géochimique à grande échelle, pour rechercher de nouveaux points minéralisés en plomb et zinc. Tous les indices connus de cette région, limitée au SE par le Massif Central, au NW par le Massif Vendéen, se trouvent dans les étages inférieurs du Lias (Domérien et parfois Hettangien).

Le principe est identique à celui qui guide les prospections alluvionnaires classiques: recherches, dans le fond des vallées recoupant les formations précédentes, de zones à fortes teneurs susceptibles de correspondre à des indices situés sur les versants.

Les réseaux hydrographiques drainant une surface de 750 km^2 ont été étudiés, par prélèvements (environ 10,000) de sols à profondeur moyenne, faits sur des profils transversaux aux vallées, distants de 250 m environ et comprenant 3 à 5 échantillons.

Cette méthode a permis de mettre en évidence quelques nouveaux indices minéralisés, qui sont actuellement étudiés par les techniques classiques et par des prospections microchimiques tactiques.

Méthodes chimiques de déterminations des éléments en traces dans les sols utilisées par le service géochimie du B.R.G.G.M. J. Beguinot, Bureau de Recherches Géologiques et Géophysiques, Paris, France.

Le B.R.G.G.M. a mis au point, en vue de la prospection microchimique, un certain nombre de méthodes de détermination d'éléments en traces dans les sols et dans les eaux: plomb, zinc, cuivre, tungstène, molybdène, antimoine, arsenic.

Le détail de ces méthodes fera l'objet d'un rapport qui etait remis aux participants lors de la présentation de la communication.

Composition isotopique de l'hydrogène de certaines eaux naturelles. René Botter, Bertrand Lazard, Guy Nief et Étienne Roth, Commissariat à l'Énergie Atomique, Gif-sur-Yvette, Seine-et-Oise, France.

Les auteurs ont comparé la composition isotopique de l'hydrogène de diverses eaux naturelles avec l'eau de Saclay prise comme référence. Ils ont pu également rattacher leurs mesures à celles d'eaux étrangères connues en valeurs absolues. Parmi ces eaux, une d'entre elles a une composition isotopique qui diffère de 30% de la composition moyenne admise à l'heure actuelle.

Alkali-metal distribution in some granites and associated hornfels. C. M. L. Bowler, Department of Geology, The University, Bristol, England.

The distribution of Li, Na, K, Rb and Cs in a suite of granites (Armorican), dykes, and both altered and unaltered country rocks from the southwest of England is being investigated. Alkali metasomatism appears to have taken place, resulting in peak concentrations in the

hornfels (originally, in the main, shales or basic igneous rocks) nearest to the contact. This effect is shown strikingly by caesium.

The composition of chondritic meteorites. Harrison Brown and Charles R. McKinney, Division of Geological Sciences, California Institute of Technology, Pasadena, California, U.S.A.

X-ray fluorescence has been applied to a study of the variations of chromium, manganese, iron, cobalt and nickel in chondrites. The regularities of the concentrations of iron, cobalt and nickel in relation to manganese and chromium indicate that there are four major families of chondrites, each of which is characterized by a specific ratio of cobalt, nickel and iron relative to chromium and manganese.

The variations of these same elements have been studied in a slab of the Gilgoin Station, New South Wales, chondrite measuring approximately 9 cm × 15 cm. Equal areas of this slab, each measuring about 1·5 cm × 2 cm, were subjected to X-ray measurement, and the variations in the composition were found to be small and about the same as the variations among all chondrites belonging to the same group. Over the entire area the concentrations of chromium and manganese were found to be nearly invariant. The extremes of the ratios Co/Cr, Ni/Cr and Fe/Cr were found to vary from the averages by ±10 per cent, ±8 per cent, and ±7 per cent, respectively. The ratio Mn/Cr varies by only ±3 per cent.

Recherche spectrographique des traces d'étain dans les sols. P. Cadiou et P. Montagne, Bureau de Recherches Géologiques, Géophysiques et Minières, Paris, France.

En vue de la prospection géochimique de l'étain, une méthode spectrographique a été élaborée, assurant une détection à moins de 20% près de ce métal dans les sols.

Les difficultés sont de plusieurs ordres. D'une part, l'étain présent dans les sols sous forme de cassitérite, dont la dureté et la densité diffèrent considérablement des grandeurs homologues relatives aux constituants des sols, doit être amené dans un état de dispersion tel que la prise d'échantillon pour spectrographie soit représentative de la substance étudiée. Ce degré de dispersion s'obtient par un broyage énergique en présence de billes d'acier; et si la dispersion des résultats analytiques augmente un peu pour des teneurs inférieures à 200 p.p.m., les mesures spectrographiques sont suffisamment reproductibles.

L'autre difficulté vient des émulsions photographiques: les plaques pour spectrographie sont de qualité trop incertaine pour qu'on puisse se servir de la caractéristique des plaques; on s'adresse à la méthode de Breckpot, qui emploie un secteur tournant, pour comparer les opacités des raies de l'étain (3175 Å) et de l'étalon interne (c'est l'or qui a été choisi, avec la raie 3122 Å). Le spectre d'arc est produit par un courant redressé de 6 A env., sur la substance additionnée de son poids de carbone pur. Spectrographe: Nelle Zélande.

On obtient ainsi les approximations: 1000 p.p.m.: 10%; 250 p.p.m.: 15%; 25 p.p.m.: 20%.

La seule difficulté de la méthode tient au broyage très poussé de la substance.

Correlation between the isotopic composition of the lead of galenas and their silver content. L. Cahen, Musée Royal du Congo Belge, Tervuren, Belgique, and P. Eberhardt, J. Geiss, F. G. Houtermans and P. Signer, Physikalisches Institut der Universität, Bern, Schweiz.

The silver content and the isotopic composition of the lead of 20 galenas from the Alps and 24 galenas from North Africa have been measured. "Model ages" are calculated from the latter.

Practically all the galenas we have investigated which have model ages comparable to the age of the host formation are found in veins, often with more or less obvious magmatic connections, and are rich in silver. The leads of the deposits located in sedimentary rocks and apparently independent of igneous activity are poor in silver and have model ages which are older than the age of the host formation.

The origin of the latter, "telethermal", deposits has often been debated, and it has been suggested that these deposits are "rejuvenated" from an older source of ore. This seems to be borne out by the fact that it is precisely deposits of this type which contain leads with model

ages older than the age of the host formation. It thus seems that the silver content together with the isotope analysis of galenas and the model age derived therefrom constitute objective criteria enabling one to distinguish which occurrences are emplaced for the first time and which are derived or rejuvenated. We have found that, with reference to the silver content, there is a sharp distinction, with little or no overlap, between leads with model ages in agreement with the age of the host formation and those with model ages older than that of the host formation.

Zur Geochemie des Titans. C. W. Correns, Sedimentpetrographisches Institut, Universität Göttingen, Göttingen, Deutschland.

Das Element Titan ist in den magmatischen Gesteinen entweder als Ion im Kristallgitter von Silikaten oder oxydischen Verbindungen eingebaut, oder als Einschluss, meist von Rutil in Quarz, Glimmern und anderen Silikaten vorhanden. Bei der Verwitterung der Silikate wird das als Ion gebundene Titan zunächst in Lösung übergeführt, scheidet sich aber sehr rasch als Oxydaquat wieder aus. Dieses wandelt sich je nach den Bedingungen in Anatas oder Rutil um. Anatas ist in organischen Säuren etwas löslich, besonders in Oxalsäure, von der bekannt ist, dass sie bei der Oxydation von Humus entsteht. Durch Auflösen und Wiederausscheiden werden in tropisch feuchten Böden, wie auf Hawaii, TiO_2-Konkretionen mit über 25% TiO_2 gebildet. Bei der Sedimentbildung gelangen die Rutilreste aus den Einschlüssen der Silikate und die aus den Ionen neugebildeten Anatase und Rutile wegen ihrer Feinkörnigkeit vorwiegend in die feinstkörnigen Sedimente, in die Tone. In den gröberen Sedimenten, in den Sanden, ist der Titangehalt im wesentlichen durch Verwitterungsreste bedingt. Auch in den Tonen mögen titanhaltige Glimmerreste noch eine gewisse Rolle spielen. In den Kalken steckt das Titan in den nichtkalkigen Bestandteilen. Auch in den Kieselgesteinen rührt der Titangehalt von den Beimengungen her, der TiO_2-Gehalt nimmt mit abnehmendem SiO_2-Gehalt zu. Selbst reine Quarzsande mit über 99% SiO_2 können noch beträchtliche Titanmengen, bis zu 0·07% TiO_2, enthalten. Diese Mengen rühren von den Einschlüssen in den Quarzen her. Auch in den Sedimenten kann durch Zersetzung der organischen Substanz TiO_2 wandern.

L'uranium dans quelques granites français; Corrélation entre l'uranium et le potassium. René Coulomb, Marcel Goldstein et Marcelle Le Mercier, Commissariat à l'Énergie Atomique, Fontenay-aux-Roses, Seine, France.

Le travail que nous présentons continue et complète une étude précédente où nous examinions les répartitions statistiques globales de l'uranium, du potassium et du sodium dans trois massifs granitiques français, (Bretagne, Vendée, Morvan).

De nouvelles analyses nous permettent de détailler les répartitions géographiques de ces trois éléments à l'intérieur de chaque massif et d'établir des corrélations entre les caractéristiques pétrochimiques et les teneurs en uranium.

Nous étudions les variations géographiques de teneurs en uranium d'une part en fonction des teneurs en potassium, d'autre part en fonction de la présence de gisements uranifères.

The distribution of gold in some basic and ultrabasic igneous rocks and minerals. J. H. Crocket, E. A. Vincent and L. R. Wager, Department of Geology and Mineralogy, Oxford, England.

Sub-microgram quantities of gold have been determined by neutron activation analysis in selected rocks from the Skaergaard gabbroic intrusion and their constituent minerals. In general, the gold content of the layered gabbros remains constant at about 0·003 p.p.m. and is evenly distributed among the various silicate and oxide phases. This, together with a consideration of oxidation potentials, suggests that gold is present as uncharged metallic atoms in the magma, rather than as charged ions or complexes, and is incorporated almost randomly into the various crystallizing phases. There is evidence of appreciable concentration of gold in the immiscible copper sulphide liquid droplets of the middle part of the intrusion, but in contrast there is no concentration in the iron sulphide droplets separating later, although gold was still available in the magma. Basalts from Halemaumau (Hawaii), the Giant's Causeway and Morven all have a gold content of 0·002 p.p.m.

The range of concentration found in six olivine-rich nodules from basalts, an Appalachian dunite and a peridotite from Rhum is from 0·0009 to 0·01 p.p.m.

The occurrence of uranium in ancient conglomerates. Charles F. Davidson, Department of Geology, The University, St. Andrews, Scotland.

In recent discussions on the origin of the mineralization of the Witwatersrand and of Blind River, various departures from actualistic principles have been postulated by geologists of the placerist school in necessary support of their views. None of these hypotheses stands up to critical examination; and from consideration of the mineralogy and geochemistry of the banket reefs it is concluded that the mineralization is certainly not of alluvial origin. Claims that detrital uraninite can be recognized in mineragraphic studies lack due objectivity. Because of reworking of the uranium and the probable presence of old radiogenic lead, it is not yet possible to place any reliance on the apparent ages recorded for these banket ores. In speculation on the source of the pay metals, it is suggested that the mineralization may be linked to periods of granitization late in the history of the Witwatersrand and Huronian geosynclines.

Signification géochimique du rapport CO_2/H_2O dans les fluides minéraux d'origine profonde. Georges Deicha, Laboratoire de Géologie Appliquée, Université de Paris, Paris, France.

Les modifications dont sont le siège les inclusions primaires des minéraux fournissent des renseignements sur certains phénomènes qui se déroulent à grande échelle dans la lithosphère: c'est ainsi que l'homogénéisation (sur la platine chauffante) d'inclusions fluides triphasées indique que CO_2 et H_2O se trouvent associés dans des rapports variés comme solvants minéralisateurs. L'expérimentation montre que condensations et distillations fractionnées scindent anhydride carbonique et eau, pour aboutir, dans les conditions physiques normales, à une séparation presque complète.

Les enseignements tirés des inclusions liquides et gazeuses de roches cristallines d'ages géologiques différents suggèrent que les apports de CO_2 et H_2O liés aux phénomènes magmatiques et tectoniques profonds ont dû jouer un rôle important dans l'évolution des enveloppes externes de notre planète (atmosphère, hydrosphère et biosphère). La comparaison de la quantité totale de CO_2 ayant participé à l'économie de ces enveloppes, à la quantité totale de l'eau qui existe à la surface du globe, donne des résultats du même ordre de grandeur que ceux de la comparaison quantitative (sur la platine réfrigérante) entre phase fugace condensée et phase aqueuse dans les inclusions de formations minérales profondes.

Étude de la radioactivité de météorites métalliques. S. Deutsch, E. Picciotto et S. Wilgain, Service de Physique Nucléaire, Bruxelles, Belgique.

Nous avons mesuré par la technique des émulsions nucléaires, la radioactivité alpha de 4 météorites métalliques: Carbo, Tamarugal, Thunda et Toluca (Hambourg).

L'absence de fading durant les 120 jours d'exposition et la contamination de surface des plaques photographiques ont été soigneusement contrôlés.

Ces échantillons de météorites ne montrent aucune activité alpha au-dessus du background des plaques—la limite supérieure de leur activité alpha est de 2×10^{-7} alpha/cm^2 sec, alors que l'activité minimum attendue d'après les concentrations en U et Th mesurées par le groupe Paneth est de 10×10^{-7} alpha/cm^2 sec.

Nos résultats indiquent que ces concentrations sont trop hautes à la fois pour U et pour Th. Une mesure radiochimique directe du Th dans ces échantillons est en cours.

Sur les variations de composition chimique pendant le metamorphisme dans le faciès des granulites. J. M. Fúster, Consejo Superior de Investigaciones Científicas, Madrid, España.

Les roches de la série des charnockites sont très bien représentées dans le massif précambrien de la Guinée Espagnole, où elles se trouvent associées avec des roches semblables dont la composition minéralogique appartient au faciès des amphibolites. On peut trouver toutes

les transitions entre les deux séries dans le même intervalle de composition. Mais c'est dans les termes les plus basiques que cette transition est évidente: il y a des filons doléritiques qui sont transformés en amphibolites dans les zones du faciès des amphibolites, et en roches noritiques dans les zones du faciès des granulites.

La comparaison entre la composition chimique des termes de la série des charnockites et de la série des amphibolites, notamment dans les termes les plus basiques, indique que, dans le processus de charnockitisation, il n'y a pas de changements importants dans la composition chimique des roches originelles, qui puissent être attribués à une basification des roches du faciès des amphibolites au passage dans les conditions du faciès des granulites.

Origine possible de certains filons uranifères français. Jacques Geffroy, Commissariat à l'Énergie Atomique, Fontenay-aux-Roses, Seine, France et Jacqueline A. Sarcia, Commissariat à l'Énergie Atomique, Razès, Haute-Vienne, France.

Les théories génétiques classiques ne peuvent pas expliquer certains gîtes uranifères français (ni leurs homologues portugais). En effet, dans le district typique du Limousin, les filons recoupent un batholithe granitique à muscovite, fait assez général en France, impliquant une relation entre ces granites (hercyniens) et les filons à pechblende. Leur localisation est atypique; le batholithe centre une zonalité du type: pegmatites (intragranitiques), filons stannowolframifères (bordiers), filons aurifères (recoupant les métamorphites encaissants). Or les filons uranifères, épithermaux, recoupent le coeur du batholithe. L'âge absolu (triasique à jurasique) est tardif par rapport à la mise en place des granites et de leur auréole minéralisée normale, définie ci-dessus. La pechblende a déposé après pénéplanation de la chaîne hercynienne, à faible profondeur. Le remplissage, à dominance lithophile (pechblende, silice, fluorine) diffère de celui des filons classiques d'Europe centrale.

Les filons limousins représentent donc des concentrations tardives, épithermales, d'éléments lithophiles. L'hypothèse suivante est proposée: Postérieurement à sa mise en place, le granite limousin a subi deux sortes de modifications, interdépendantes: (1) chimiques: muscovitisation, albitisation, phyllitisation, aboutissant à une "libération" in situ de l'uranium normal du granite; (2) mécaniques: mylonitisations, favorisant les circulations capables d'extraire, puis de concentrer dans des fractures, les éléments lithophiles facilement solubles (dont l'uranium).

L'hypothèse proposée permet d'envisager l'existence de filons de basse température, n dépendants du cortège minéralisé normal d'une orogenèse (ou d'une "régénération").

La prospection geochimique des gisements de molybdénite dans les Monts Drocea. D. Giusca, Comité géologique de la République Populaire de Roumanie, Bucuresti, Roumanie.

Les gisements de molybdénite de Roumanie sont associés aux massifs de granites et granodiorites laramiques. Près de Săvîrșin et de Cerbia (Monts Drocea) on trouve des filons relativement courts, d'épaisseur variable, constitués de quartz, pyrite et molybdénite. La teneur en molybdène varie largement et les moyennes des différents filons oscillent entre 0·17 et 0·9% Mo. Rapportée au mètre carré de surface, la variation est moindre, de 1·8 à 4·5 kg Mo. Une minéralisation exclusivement pyriteuse, ultérieure, accompagnée d'intenses phénomènes de séricitisation a une plus grande extension. Il s'ensuit que les phénomènes autométamorphiques ne sauraient être utilisés comme indicateur de prospection. Etant couverte par un sol de forêt peu épais, la région se prête aux recherches géochimiques.

Près de Săvîrșin, nous avons prospecté la surface d'affleurements de la granodiorite. Les échantillons ont été prélevés d'une profondeur moyenne de 30 cm, suivant un réseau de 10 m × 10 m. Le dosage du Mo a été effectué par colorimétrie. Le fond de la carte géochimique correspond aux teneurs de 0–1 p.p.m., les zones anormales aux teneurs de 3–8 p.p.m., atteignant plus rarement 20–22 p.p.m. Ces zones ont été vérifiées à l'aide de tranchées ou de travaux souterrains, ce qui a permis d'identifier les filons dans la plupart des cas. La forme des anomalies est parfois très suggestive, correspondant exactement à la localisation des filons. On constate

encore un parallélisme remarquable entre les valeurs maxima des zones anomales et le contenu en Mo par métre carré.

Measurement of chemical activity of subterranean waters; Mud activity tester. M. Gondouin, Schlumberger Well Surveying Corporation, Ridgefield, Connecticut, U.S.A.

Among the various logging techniques applied to oil exploration, the SP log in particular is used to determine the resistivity of the formation waters, which itself is derived from the value of the activity. The amplitude of the SP is governed primarily by the activity ratio of the formation water to the mud filtrate. In order to obtain the correct value of the water activity from the SP log, it is therefore necessary to know first the activity of the mud filtrate. This quantity often cannot be obtained with sufficient accuracy from either routine chemical analyses or resistivity measurements.

This paper describes a technique and apparatus for the direct determination of mud activity based on the measurement of the membrane potential developed between the mud and a standard NaCl solution of known activity when separated by a cation exchange membrane. The cation exchanger responsible for the SP phenomenon in the ground is shale, but the use of an actual shale membrane was ruled out because of its fragility. Instead, a suitable synthetic ion exchange membrane was selected.

The membrane has been incorporated in a cell designed for field use. The measuring electrodes are Ag/AgCl, and the e.m.f. of the cell is measured with either a potentiometer circuit or a battery-operated commercial electrometer. Measurement requires only a few minutes.

Mise en évidence de structures par prospection microchimique tactique. C. Granier, Bureau de Recherches Géologiques et Géophysiques, Paris, France.

Lors d'une recherche d'extension d'un gîte minéralisé en plomb et zinc, la prospection microchimique a été utilisée pour retrouver le passage d'accidents, le long desquels la minéralisation se trouve localisée dans des horizons préférentiels et qui affectent non seulement ces horizons, mais des terrains de recouvrement d'épaisseur et de nature variables.

Dans les zones de faible recouvrement, l'accident recherché se traduisait par une anomalie (300 à 400 p.p.m.) nettement différenciée de la teneur du fond (100 p.p.m.).

La méthode a été ensuite appliquée dans un secteur où les terrains de couverture ont une puissance très supérieure.

La différence entre teneurs normales et anormales ayant une amplitude moindre, un soin particulier a dû être apporté à l'exécution des opérations chimiques de façon à mettre en évidence des différences de teneurs de l'ordre de 20 p.p.m.

C'est par le tracé des courbes d'isoteneurs de 75 et 100 p.p.m. pour un fond de 25 à 50 p.p.m. que le passage de l'accident recherché a été localisé.

Des sondages implantés d'après les résultats de cette prospection ont effectivement retrouvé cet accident d'ailleurs minéralisé.

Distribution of some trace elements in eclogites and ultrabasic rocks of the Münchberg gneiss in Fichtelgebirge. Paula Hahn-Weinheimer, Mineralogisches Institut der Universität, Frankfurt/M, Deutschland.

Lens-shaped masses of serpentinite and eclogite occur parallel to the main direction of strike in the Münchberg gneiss. The lenses are arranged in three parallel sequences, two of them being situated in the gneiss itself, while the third lens lies within the border zone. The abundance of the accessory elements Cr, Ni, Co, Mn, Sc, V, Ti, Ba and Sr shows larger variations in the serpentinites of the border zone than in the central serpentinites. In the latter, preferably Pt and Pd are present (0·005–0·05 p.p.m.). The picrites in the Paleozoic formations on the northern border of the gneiss are different from the serpentinites, and in them the platinum metals are absent.

The platinum metals were concentrated by means of quinoline-selenol-2, which proved to be the most sensitive compound among a number of heterocyclic compounds containing S and Se.

All samples were analysed spectrochemically. The sensitivity of this method is 0·1 γ in 100 ml.

Direct genetic connections between the eclogites and their primary rocks are difficult to find. The total chemical composition and the accessory elements suggest that the largest eclogite complex and a metagabbrodiorite in its vicinity may have common origin.

The determination of elementary carbon yielded contents of 0·1–0·5 per cent C in some eclogites. The graphite carbon and the carbonate carbon have very similar $^{12}C/^{13}C$ ratios, closely resembling those of Precambrian schists. The serpentinites contain 0·003–0·03 per cent C, and talc and chlorite schists $<0·001$ per cent C.

Urangehalte österreichischer Gesteine und Wässer. F. Hecht, II. Chemisches Universitätsinstitut, Wien, Österreich.

In verschiedenen österreichischen Wässern und Gesteinen wurden Uranbestimmungen ausgeführt. Natürliche Wässer aus dem Einzugsgebiet der Donau, dem niederösterreichischen Waldviertel (böhmischer Kristallin) und dem Burgenland (Ostösterreich) zeigten Urangehalte von 0·2 bis über 3 μg U/l. (3×10^{-9}). Dabei erwies sich, dass im böhmischen Kristallin Bäche und Flüsse nur niedrige Urankonzentrationen haben (etwa 0·5 μg/l.), dass also dort nurger inge Auslaugung stattfindet. Hingegen enthalten diejenigen Bäche und Flüsse, die durch Sedimentzonen von Sandstein, Flysch und Molasse führen, höhere Urankonzentrationen bis 3 μg/l. Die Urankonzentration der Donau selbst beträgt rund 1·5 μg/l. Der Neufeldersee, ein ertrunkenes ehemaliges Braunkohlenbergwerk an der Grenze zwischen Niederösterreich und Burgenland, hat 4 bis 5 μg U/l.

Sande aus Nebenflüssen der Donau führen bis 7 g U/to. Es gelangen aber Anreicherungen bis zu 200 g U/to.

In einem Granosyenitgneis aus Kärnten wurden 22·5 g U/to gefunden, das Mehrfache des durchschnittlichen Urangehaltes saurer Erstarrungsgesteine.

Erdöle aus dem Wiener Becken (Rohöle) enthalten fast 20 μg U/l., die Destillationsrückstände einer Raffinerie bis 2 g U/to, was eine Anreicherung bedeutet, aber nicht für eine Ausbeutungswürdigkeit hinreicht. Erdölsondenwässer zeigten Urangehalte, die denjenigen des Ozeanwassers (3 μg/l.) gelegentlich übertrafen.

Österreichische Braunkohlen (Trimmelkam) enthalten bis zu mehreren hundert Gramm Uran/Tonne Asche, was diese Aschen ausbeutungswürdig scheinen lässt.

Die Analysenmethodik war die früher beschriebene (F. Hecht, J. Korkisch, R. Patzak und A. Thiard, *Mikrochim. Acta* 1956, S.1283).

Die Datierung Re-haltiger Mineralien mittels Neutronenaktivierung und zur Bestimmung der Halbwertszeit des natürlich β^--aktiven ^{187}Re. W. Herr und E. Merz, Max-Planck-Institut für Chemie, Mainz, Deutschland.

Erst das Auffinden eines Folgeproduktes vom β^--aktiven Rhenium zeigte, dass diese natürliche Radioaktivität relativ intensiv ist. Da einer physikalischen Strahlenmessung grosse Schwierigkeiten entgegenstanden und diese vorerst wegen der extrem weichen Strahlung kaum zu einem verlässlichen Wert für die Halbwertszeit des ^{187}Re führen kann, wurde auf radiochemischem Wege versucht, den Gehalt an Rhenium und an Tochterisotop ^{187}Os in Mineralien von bekanntem Alter quantitativ zu erfassen. Die Bemühungen zeigten, dass eine geologische Datierung von Re-haltigen Mineralien, insbesonders von Molybdänglanzen, möglich ist, und dass die natürliche Radioaktivität des Re zur Grundlage einer neuen Methode der Altersbestimmung gemacht werden kann. Es werden die ausgearbeiteten radiometrischen Bestimmungsverfahren für Re und Os und speziell die Ermittlung der Isotopenzusammensetzung des Os angegeben. Die Ergebnisse an mehr als 20 Mineralproben von den verschiedensten Fundplätzen belegen die Leistungsfähigkeit der neuen Datierungsmethode, die gerade dort eine Lücke zu schliessen vermag wo andere radioaktive Methoden nicht anwendbar sind. Die Aufstellung einer relativen Altersskala der untersuchten Mineralien und der Vergleich von Datierungen, die auf anderem Wege an Gesteinen der gleichen Lagerstätte vorgenommen wurden, gestattete es nunmehr, die Halbwertszeit des ^{187}Re in sehr enge Grenzen zu legen.

Search for decay products of natural technetium. W. Herr and E. Merz, Max-Planck-Institut für Chemie, Mainz, Deutschland, and P. Eberhardt, J. Geiss, C. Lang and P. Signer, Physikalisches Institut der Universität, Bern, Schweiz.

Evidence from neutron-activation experiments for the terrestrial occurrence of ^{98}Tc has been given recently by several authors. In order to get an independent check on these findings, a search for the possible decay products of ^{98}Tc and also of ^{97}Tc has been carried out.

Ruthenium was extracted from about 24 kg of Precambrian columbite, gadolinite and tantalite samples. The isotopic composition of the ruthenium was measured and compared with the isotopic composition of ruthenium from the Carbo iron meteorite. From the mineral samples mentioned, about 10 kg which proved to have a lower than average molybdenum content was selected for the isotope analysis of molybdenum. For comparison, molybdenum from molybdenite was analysed. No enrichment of the isotopes ^{97}Mo, ^{98}Mo, and ^{98}Ru was found in the mineral samples.

The ruthenium and molybdenum content of the samples, viz.,

Material	Ru g/g	Mo g/g
Columbite, gadolinite, tantalite	$(1{\cdot}0 \pm 0{\cdot}1) \times 10^{-9}$	$(1{\cdot}0 \pm 0{\cdot}2) \times 10^{-7}$
Carbo iron meteorite	$(52{\cdot}4 \pm 1{\cdot}5) \times 10^{-6}$	

yields the upper limits for a radiogenic proportion of the isotopes in question as

^{97}Mo radiogenic $1{\cdot}2 \times 10^{-10}$ g/g

^{98}Mo radiogenic $1{\cdot}5 \times 10^{-10}$ g/g

^{98}Ru radiogenic $2{\cdot}0 \times 10^{-12}$ g/g

The significance of these figures relative to the terrestrial occurrence of natural long-lived technetium is discussed.

Détermination des constantes de désintégration du ^{176}Lu par la démonstration du produit de désintégration ^{176}Hf. W. Herr et E. Merz, Max-Planck-Institut für Chemie, Mainz, Deutschland, et P. Eberhardt et P. Signer, Physikalisches Institut der Universität, Bern, Schweiz.

Des mesures directes de la constante de désintégration du ^{176}Lu faites par différents auteurs avec des compteurs ont fourni une valeur de la constante entre $9{\cdot}5 \times 10^{-12}$ a^{-1} et $3{\cdot}2 \times 10^{-11}$ a^{-1}.

Nous avons déterminé quantitativement du Hf et du Lu d'un gadolinite et d'autre part nous avons mésuré l'âge de ce minéral par la méthode du RaD et la méthode du ^{207}Pb/^{206}Pb. Pour la méthode analytique du Hf et du Lu nous avons fait usage des colonnes des échangeurs de ions au moyen des indicateurs radioactif et par l'activation par des neutrons.

Un examen de la composition isotopique indiquait un pourcentage de $45 \pm 1\%$ de ^{176}Hf radiogène. Cette valeur se trouve en bon accord avec les résultats obtenus par l'activation par des neutrons. Le minéral a un âge de 830 ma, d'où l'on déduit avec les valeurs analytiques pour le pourcentage du Lu et du Hf: $\lambda_{\beta^-} = 3{\cdot}1 \pm 0{\cdot}5 \times 10^{-11}$ a^{-1}.

Une détermination de la relation $\lambda_K/\lambda_{\beta^-}$ par la détermination du ^{176}Yb d'origine radiogène promet peu de succès, puisque Yb est plus abondant que Lu et, qu'en outre, ^{176}Yb représente le 12·7% du Yb et que ^{176}Hf ne représente que le 5·12% du Hf ordinaire.

Il semble possible d'utiliser cette méthode de détermination d'âge des différents minéraux dont le pourcentage de Lu est élevé, tandis qu'en même temps le pourcentage de Hf est insignifiant.

Some applications of thermodynamics to problems in economic geology. H. D. Holland, Department of Geology, Princeton University, Princeton, New Jersey, U.S.A.

The stability fields of the oxides and sulphides of fifteen metals have been plotted in three-dimensional diagrams in which the logarithms of the oxygen fugacity and of the sulphur fugacity comprise the two horizontals axes, and in which temperature is plotted along the vertical axis. It is shown that on the basis of this type of diagram, mineral assemblages are predicted which are consistent with observations on metallic ore deposits. Many of the commonly observed mineral assemblages are found to lie along a "main line of descent" in this type of diagram. The observed descent can be understood in terms of classical ideas on the origin of hydrothermal ore deposits, and is used to derive fugacity data for a number of important volatile constituents in ore-forming fluids. The relationship between the calculated fugacities and the pressure of the volatile components of ore-forming fluids is outlined.

Data of rock analyses; Progress report (1957). Marjorie Hooker, U.S. Geological Survey, Washington 25, D.C., U.S.A.

In 1952, the U.S. Geological Survey undertook the compilation of chemical analyses of igneous and metamorphic rocks from the world literature for the years 1914–1953. The first progress report, outlining the scope and procedures of the work, was given at the meeting of the Commission on Geochemistry (IUPAC) in Zurich in August 1953. The second progress report was presented at the 20th International Geological Congress in Mexico City in September 1956, and will be published in the Proceedings of the meetings.

The systematic examination of the literature, based on a comprehensive list of more than 1600 periodicals and serials and several hundred books, is being conducted on a regional plan. Completed at this time are the publications of Africa, New Zealand, and Australia. Annotated and indexed references from the African and New Zealand publications have been published in *Geochimica et Cosmochimica Acta*. In process is the examination of the literature of the United States, Great Britain, and Germany, a considerable part of which has been completed. Publication of any part of the analyses will not be attempted before examination of the literature is completed; the bibliographic data are being published as sections are completed in order to make the source material more readily available.

Compilation of the analyses from the literature is proceeding simultaneously, although it does not necessarily keep pace with the examination of the literature. At this time, approximately 2500 analyses have been placed in the files and can be consulted in several ways.

Geochemistry of some Swiss granites. Th. Hügi, Mineralogisches Institut, Universität Bern, Bern, Schweiz, and D. J. Swaine, The Macaulay Institute for Soil Research, Craigiebuckler, Aberdeen, Scotland.

An investigation, based on petrological field observations and laboratory work, has been carried out on granites belonging to the Hercynian Aar Massif in the Swiss Alps. Granitic rocks make up 51 per cent of the surface of this autochthonous massif. Some of these granites are believed to be of early Hercynian age, and others were formed during the late Carboniferous or early Permian. These older granites show contamination by gneissic material from surrounding rocks. Such pre-Hercynian gneisses were formed from the oldest sediments of the Aar Massif. Field observations, petrological evidence, and trace-element data prove strong contamination of the so-called Lauterbrunner granite and the Innertkirchner granite. The contamination increases towards the east of the massif, and the gneisses and contaminated granites have higher contents of some metals (for example Cr and V). Younger granites, for example the Central Aare granite and the Mittagfluh granite, are lower in Fe, Mg, and Ca but slightly higher in Si and K than the older granites and do not show any contamination.

Average values for the trace-element contents of the Aar Massif granites are compared with published values for other granites. The trace-element data are discussed, and histograms are shown for several elements (number of samples plotted against contents). Reference is made to the concentration of some trace elements in rare minerals occurring in cavities.

Geochemical investigations of geysers in Japan. Iwaji Iwasaki, Laboratory of Analytical Chemistry and Geochemistry, Tokyo Institute of Technology, Tokyo, Japan.

There are more than ten geysers and many intermittent springs in Japan, some of which are natural and the others obtained by boring. The geysers seem to be a special case in intermittent springs, but we have not found any essential differences of chemical properties of waters and gases emitted between various types of geysers and common hot springs in Japan with the exception of periodic variation of amount, temperature, and chemical properties of waters and gases emitted from geysers. From these facts we can conclude that the chemical properties of waters and gases emitted from geysers are not so important as the structure of geyser systems or the periodic phenomena of geysers. From this point of view, we have studied theoretically the nature of various types of geyser models with cavities and various types of geysers in Japan. From these model experiments, the relations among rate of water supply, rate of water discharge during eruption and eruption period, the meaning of the so-called "overflow phenomenon of hot water", or "preliminary minor ebullition and preliminary small spouting", which are thought to be always accompanied with the geyser phenomenon, and the variations in chemical composition, or the origin of the waters and gases emitted in all eruption periods, are clarified.

A geochemical hypothesis of the structure of the Earth. A. F. Kapustinsky, Institute of General and Inorganic Chemistry, Academy of Sciences of the U.S.S.R., Moscow, U.S.S.R.

Data on atomic structure, quantum mechanics, crystal thermodynamics, and seismology indicate that the two extreme hypotheses of the structure of the Earth, viz. Goldschmidt's hypothesis of the layered structure and Lodochnikov's hypothesis of a homogeneous globe, are both erroneous. It is suggested that the "solid" globe consists of three geospheres, viz., the centrisphere, the intersphere and the perisphere. The centrisphere, which starts at a depth of 2900 km, is isothermal (2000°C) and consists of a completely metallized zone where no chemical reactions take place. The intersphere is characterized by chemically degenerated atoms resulting from the transition of electrons, "smashed in" by high pressure, to internal energy levels the formation of which has not yet been accomplished. Only in the relatively thin (60–120 km from the surface) perisphere do common chemical reactions take place. The perisphere may be called the zone of normal chemistry. The transformations of matter producing rocks, ores and minerals take place chiefly in the perisphere.

Fixation of oxides of potassium and sodium in the montmorillonite group of layer silicates. Joseph Alton Kornfeld, 610 Mid-Continent Building, Tulsa, Oklahoma, U.S.A.

Potassium is mutually soluble with sodium at high magmatic temperatures, but at low temperatures, isomorphic substitution between the two metals is greatly restricted. In magmatic rocks, potassium predominates over sodium. However, retention of potassium in the soils results in an excess of sodium over potassium in lake and river waters. Additional concentration of potassium by clay particles in fine fractions of marine sediments results in extreme domination of sodium over potassium in ocean water.

Fixation of sodium in clay minerals is controlled mainly by precipitation, drainage and evaporation. Chemical decomposition during weathering and later cation-exchange reactions with circulating solutions further affect the greatly reduced fixation of sodium in clay minerals.

Preferential permanent fixation of potassium over sodium is characteristic of cation-exchange reactions in clay minerals. The degree to which silicon is replaced by aluminium in the silicon–oxygen tetrahedra strongly affects the other structural sites in the minerals and the relative abundance of potassium and sodium. Octahedral sites in layer silicates are preferentially filled by Fe, Mg and Al, according to the electronegativity of these three metals and of oxygen atoms surrounding the sites.

Potassium and sodium both occupy interlayer ionic positions and are additive to the value of the interlayer ion which must satisfy the electrostatic charges in the structure.

Recent developments in geochemistry. J. Laurence Kulp, Lamont Geological Observatory, Columbia University, Palisades, New York, U.S.A.

New measurements of the age of metamorphic areas by the rubidium–strontium, potassium–argon and uranium–lead methods at the Lamont observatory have shed considerable light on the reliability of these methods and their relative sensitivity to the thermal history of their environment.

Intensive work on several regions has shown that large areas such as the area of the Bighorn uplift of Wyoming and Montana, the area of south-east Manitoba into south-east Minnesota, and the New Jersey–New York highland may be underlain by a rock complex reflecting a single metamorphic event.

The potassium–argon method yields low ages in feldspar and fine-grained micas. For very old book mica there is also evidence for argon loss, but as yet it cannot be proved as due to continuous diffusion at low temperature. The rubidium–strontium method is least sensitive to loss of the radiogenic daughter and is generally useful in establishing absolute ages.

Sur le comportement géochimique du titane dans certaines séries cristallophylliennes. P. Lapadu-Hargues, Faculté des Sciences, Clermont-Ferrand, France.

Le titane est un des plus importants parmi les oligoéléments de la lithosphère. Grâce aux analyses déjà existantes, grâce également à une série d'analyses nouvelles relatives, d'une part à des roches métamorphiques du Massif Central français, d'autre part à des granites de cette même région, on a plus spécialement ici tenté de dégager la répartition générale de cet élément dans certaines séries métamorphiques.

A l'aide des résultats obtenus, l'auteur propose de discuter le comportement du titane au cours des processus du métamorphisme; les deux hypothèses possibles, soit stabilité du titane qui resterait dans la roche primitive, soit départ ou apport éventuels, sont présentées. En conclusion, on tente de montrer qu'en certains cas, la titane pourrait peut-être donner des indications sur la roche primitive à partir de laquelle le schiste cristallin s'est constitué.

La caractérisation géochimique des phases métallogénétiques des gîtes hydrothermaux. F. Leutwein, Mineralogisches Institut der Bergakademie, Freiberg/Sa., Deutschland.

Le district filonien minéralisé de Freiberg, dans son étendue et sa complexité, a permis d'étudier la manière de différencier les diverses phases d'un cycle métallogénétique à l'aide des éléments en traces.

De chaque d'essai, on doit isoler avec le plus grand soin, avec l'aide du microscope de préparation, les minéraux ayant un intérêt, et déterminer dans chacun d'eux les éléments en traces, qui s'y trouvent. Les études de la galène montrent, par exemple, qu'ici la teneur en bismuth (sous forme d'inclusions isomorphes de schapbachite, $AgBiS_2$) est clairement fonction de la profondeur de formation, de sorte que les lignes d'égale teneur en Bi permettent de reconstruire les surfaces isothermes au moment du dépôt de la minéralisation. De telles reconstructions, on peut déduire des informations sur la distance relative du magma générateur au moment du dépôt, sur les réajustements tectoniques, ainsi que des indications sur l'exploitabilité du filon dans les parties plus profondes.

L'exemple des blendes montre qu'ici la teneur en fer ne change pas avec la profondeur, tandis que celle en cobalt augmente avec la profondeur et celle en étain augmente au contraire dans les zones moyennes et jusque dans les zones supérieures.

Pour les diverses générations de carbonates (ankérite, etc.) une différenciation s'obtient à l'aide des teneurs en Mg, Fe, Mn, ainsi que de celles en oligo-éléments Ba et Sr. Les barytines aussi se différencient de façon analogue par les variations de leurs teneurs en Sr et Ca.

Bibliographie des analyses de roches. J. Lombard, Bureau d'Études géologiques, Paris, France.

La Commission de la Carte géologique du Monde, présidée par M. F. Blondel, a demandé en 1955 à tous les Services géologiques de lui envoyer la liste des publications parues depuis 1920 et contenant des analyses de roches de leur pays.

Trente neuf pays ont répondu à cet appel. Leurs réponses constituent une documentation très importante. Elle sera envoyée à tous les Services qui y ont collaboré. D'autre part, elle sera mise à la disposition du M. Earl Ingerson et de Mlle. Marjorie Hooker pour le travail qu'ils ont entrepris sur le même sujet.

Évolution naturelle des huiles brutes. M. Louis et F. Bienner, Institut français du Pétrole, Rueil-Malmaison, Seine-et-Oise, France.

Des exemples sont cités de transformation d'un pétrole en malthe, et d'un pétrole en asphalte.

Outre le changement de constitution, la nature chimique évolue aussi. En particulier on observe une diminution des carbures paraffiniques principalement de ceux à poids moléculaires moins élevés.

La composition chimique des roches et les formes du relief terrestre. M. Matschinski, Centre National de la Recherche Scientifique, Paris, France.

L'auteur étudie les données de plus de 80 explorateurs concernant les teneurs des oxydes: SiO_2, Al_2O_3, CaO, MgO, Na_2O, K_2O, FeO + Fe_2O_3 pour 255 roches appartenant à 15 arcs volcaniques (179 volcans actifs et une quantité encore plus grande d'éteints). Il compare ces données aux densités des volcans sur ces arcs (dans le sens de Sapper) et le "rayon cartographique" des arcs. Ces données ont permis d'établir l'existence d'une corrélation entre les teneurs des oxydes sus-indiqués (qui forment, comme il est bien connu, plus de 90% de la masse de la Terre) d'une part et de la densité et du rayon cartographique d'autre part. L'auteur a calculé aussi les positions approximatives des lignes de régression qui sont données dans les figures représentant les corrélations découvertes.

L'auteur donne également des autres exemples des corrélations entre composition chimique des roches et les formes du relief terrestre. Il considère enfin quelques explications possibles de ce genre des corrélations.

Considérations statistiques sur la distribution des roches sur la surface terrestre. M. Matschinski, Centre National de la Recherche Scientifique. Paris, France.

Sur la base de ses travaux antérieurs*† l'auteur établit une loi statistique très générale qui détermine la distribution des roches sur la surface terrestre.

La distribution des minerais de basse et de haute température de formation. W. Nieuwenkamp, Mineralogisch-Geologisch Instituut der Rijks-Universiteit te Utrecht, Utrecht, Nederland.

Le magmatisme classique (Rosenbuschien) voit le magma s'introduire dans des formations quelconques en apportant les éléments formateurs des gisements de minerais. Plutôt que les volcans ce sont les roches de profondeur qui montrent un rapport avec la minéralisation.

Les théories moins tranchées sur la mise en place de celles-ci, et où la coopération de sédiments entre en jeu, mènent à des interprétations métallogéniques plus naturelles.

Pour tous les éléments à faible concentration dans l'eau de mer, la teneur moyenne des magmas sera égale à, ou surpassée par celle des sédiments. Le rôle des agents pétrogénétiques se borne à provoquer une concentration d'éléments selon leur degré de mobilité, principe illustré par l'exemple de la répartition des sulfures de mercure et de molybdène.

Les facteurs physiques déterminant la formation des schistes cristallins. N. Oulianoff, Laboratoire de Géologie, Université, Lausanne, Suisse.

Les dépôts sédimentaires représentent la matière première principale des schistes cristallins. La diagénèse est le premier échelon du métamorphisme. Ce dernier se définit comme l'adaptation

* Énergie nécessaire pour la dessiccation des sols et coefficients de forme correspondants. *Ann. Geophys.* **11**, p. 481, 1955.

† Sur une loi générale de la distribution des roches. Communication faite à la Société française de Géochimie, novembre 1955.

par recristallisation, des masses rocheuses, aux nouvelles conditions physico-chimiques. Cette recristallisation entraine le changement de la composition minéralogique, ou de la structure, ou des deux ensemble. On considère, ordinairement, deux espèces de facteurs physiques: chaleur et pression. La plus grande partie des schistes cristallins résulte du métamorphisme général ou régional. Mais la température augmente lentement avec la profondeur. La pression dépendante du poids des couches est dirigée dans les zones supérieures, mais se transforme rapidement, avec la profondeur, en pression hydrostatique, et perd ainsi son efficacité. Ces deux facteurs physiques produisent des effets relativement faibles sur le chimisme des masses rocheuses.

Les phases fluides seules sont capables de déclancher des réactions chimiques énergiques avec le milieu solide. Dans les sédiments, la phase fluide existe sous forme d'eau. Il s'agit principalement de l'eau de mer, véritable "plasma" qui retient en solution nombreux et divers ions. Mais cette eau étant emprisonnée, "fossilisée" se trouve à l'état statique au stade initial. Il faut qu'elle soit "remise en mouvement" pour qu'elle entre en contact avec divers matériaux des couches sédimentaires. Alors les fluides deviennent actifs et déterminent la formation de nouvelles combinaisons cristallines. Cette remise en mouvement se réalise à la suite des orogénèses. Dans les zones atteintes par les orogénèses réitérées, le métamorphisme se manifeste avec une énergie accrue.

Sur la dissolution à chaud du carbonate de calcium. Janine Rasumny, Laboratoire de Géologie, École Normale Supérieure, Paris, France.

Des travaux ont été effectués, qui peuvent être décrits en rappelant la communication de M. Schloesing (*C. R. Acad. Sci. Paris* **74,** p. 1552, 1872): "Les expériences que j'ai eu l'honneur de communiquer à l'Académie établissent que l'eau pure, mise en présence de carbonate de chaux et d'une atmosphère contenant une proportion déterminée d'acide carbonique, dissout à la fois du gaz carbonique libre (selon la loi d'absorption des gaz), du carbonate neutre, selon la solubilité de ce sel dans l'eau exempte d'acide carbonique, et du bicarbonate de chaux."

Alors que les travaux de Schloesing ont été effectués à froid, nous avons étudié la dissolution à chaud, dans un soxhlet, de différentes roches calcaires soumises à l'attaque pendant une semaine. Il est entendu que le gaz carbonique se dégage dès le début de l'opération. Les dosages sont effectués à l'aide du versénate, en utilisant les deux procédés suivants: pour le magnésium, par la méthode de M. Mestayer; pour le calcium, par la méthode de M. Charlot.

The role of resistates in the geochemical cycle of thorium and uranium. John J. W. Rogers and John A. S. Adams, Department of Geology, The Rice Institute, Houston, Texas, U.S.A.

The role of resistates in the geochemical cycle of thorium and uranium can be estimated by the following independent lines of evidence: (1) geochemical balances based on the determination of thorium and uranium in average igneous and sedimentary rocks; (2) autoradiography; (3) mineral separations; (4) leaching studies. A synthesis of published data together with nearly 300 new determinations indicates that for all rocks a minimum of half of the thorium and a minimum of one-third of the uranium is held in resistates. The geochemical balances between igneous and sedimentary rocks are as follows:

	Igneous rocks	Sedimentary rocks		
		Shales	Sandstones	Limestones
Weight per cent	100	46–?	32–?	22–?
Th in p.p.m.	13·5–1·5	12–1	24–7	1·7–0·7
U in p.p.m.	3·5–0·5	3·7–0·5	4·1–1·5	2·2–0·1

Prospection microchimique du tungstène dans le Limousin. W. Sakowitsch, Bureau de Recherches Géologiques et Géophysiques, Paris, France.

Dans le cadre des recherches effectuées par le B.R.G.G.M. dans la chaîne des Blonds (NW du Massif Central), sur des formations filoniennes minéralisées en wolfram, des déterminations systématiques de la teneur en tungstène dans les sols ont été effectuées par la méthode au dithiol. Les techniques de prélèvement furent les suivantes: (a) Pour des recherches de détail: des prélèvements tous les 5 ou 10 m, sur des profils distants de 10 à 20 m, implantés perpendiculairement aux directions des filons déjà reconnus, ont permis d'en retrouver la prolongation et de mettre en évidence des formations parallèles. (b) Pour une reconnaissance à plus grande échelle: prélèvements tous les 20 m, sur des profils distants de 80 m, puis dans les zones à fortes teneurs sur des profils intermédiaires situés à 40 m des premiers.

Cette méthode a permis d'éliminer les 4/5 de la surface de 2 km^2 ainsi prospectée, tout en localisant les secteurs sur lesquels doivent porter les études ultérieures.

Le chimisme des roches à manganèse du Cristallin des Carpates Orientales et Méridionales de la Roumanie. Mircea Savul, Université de Jassy, Roumanie, et Virgil Ianovici, Université de Bucarest, Roumanie.

Dans le Cristallin des Carpates de Roumanie on rencontre un certain nombre de gisements à roches manganésifères. Ces roches considérées comme sédimentogènes, ont été métamorphisées ultérieurement, de même que les schistes aves lesquels elles se trouvent associées. On a étudié les roches à manganèse de Răzoare et de Sarul Dornei-Iacobeni, dans les Carpates Orientales, ainsi que celles des Monts de Sebeș, de Delinești et de Globu Rău, dans les Carpates Méridionales.

Les auteurs étudient ces roches à manganèse du point de vue géochimique. Afin d'identifier les grands traits du chimisme de ces roches et d'éliminer les traits accidentels, ils appliquent la loi des grands nombres, en utilisant plusieurs milliers de données analytiques concernant SiO_2, MnO, FeO, CaO, P_2O_5 et S. On a construit également de nombreux diagrammes: courbes de fréquence, diagrammes de variation par classes de 5% SiO_2, diagrammes SiO_2—MnO—FeO etc. montrant un caractère de continuité pour tous les gisements étudiés.

On constate une grande unité en ce qui concerne le type de genèse, les variations étant dues aux modifications locales des conditions de genèse, et en même temps un rapprochement assez étroit entre le chimisme des roches à manganèse des Carpates Méridionales et celles des Carpates Orientales.

On calcule la composition moyenne des roches à manganèse des Carpates, selon des classes à 5% SiO_2.

Les résultats obtenus dans cette étude peuvent servir de base pour une interprétation géochimique générale des gisements de manganèse des schistes cristallins.

Étude des solutions des sols et des eaux des nappes phréatiques sous-jacentes. Marc Schoeller, Laboratoire de Géologie de l'Université, Bordeaux, France.

L'étude a porté principalement sur les sols podzoliques et les sols bruns des environs de Bordeaux. Elle a mis en évidence:

(1) La composition chimique des solutions varie dans un même sol, en fonction de l'horizon pédologique. Les phénomènes de dissolution, de précipitation, d'échange de bases, de dilution et d'évapo-transpiration en sont les principaux facteurs.

(2) La composition chimique des solutions varie en fonction de la nature pédologique. Ainsi les solutions des podzols se différencient de celles des sols bruns par une concentration et des rapports HCO_3/Cl, Ca/Cl, Ca/Na plus faibles, ce qui est dû à une mise en solution beaucoup plus facile de nombreux éléments dans les sols bruns.

(3) La composition chimique des solutions des sols est tout à fait semblable à celles des eaux des nappes phréatiques sous-jacentes; et entre les eaux des solutions des sols bruns et des sols podzoliques, il y a la même différence qu'entre les eaux des nappes phréatiques situées dessous.

Alkali metals in Norwegian feldspars. Ross Taylor, Knut Heier and Stephen Moorbath
Department of Geology and Mineralogy, Oxford, England.

Lithium, rubidium and caesium were determined spectrochemically in fifty feldspars, using sodium as a variable internal standard. Sodium and potassium were determined by flame photometry. The samples are from different types of gneisses, granites and pegmatites from the Pre-Cambrian of southern Norway. The potassium/rubidium ratios are normal, except in some pegmatites where rubidium enrichment occurs. A general correlation of the distribution of lithium and caesium in various rock types is presented.

The petrochemistry of the Oslo-Fen petrographical province. S. I. Tomkeieff, Department of Geology, King's College, University of Durham, Newcastle upon Tyne, England.

A detailed survey of the field occurrence and distribution and of the petrographical and chemical characters of the Oslo district igneous rocks suggests that they belong to three distinct magmatic sources: basic, intermediate-acid, and acid. This primary differentiation was probably achieved through a selective remelting of the different zones of the Earth's crust. Prior to and during eruption each of the magmas underwent diffusion-differentiation and crystallization-differentiation processes which gave rise to a large number of rock types. By means of scatter, point, and linear diagrams these rock types can be systematically ordered, and family relationships and trends of differentiation can be followed.

The Fen district, situated outside the Oslo graben, probably represents a deep level of a diatreme in which the following genetic stages are represented: (a) Differentiation series urtite—ijolite—melteigite—jacupirangite, derived from alkali pyroxenite, in itself a differentiate of the Oslo basic magma. (b) Differentiation series juvite—tinguaite—malignite—tveitåsite, a hybrid alkali syenite magma produced by the action of the alkali pyroxenite magma on the country rock. (c) Residual carbonatite series: calcium series, varying from calcite melteigite (hollaite) to calcite carbonatite (sövite), and magnesium series varying from damtjernite to dolomite carbonatite (rauhaugite). (d) Iron-ore series. (e) Fenitized country rock (granite gneiss).

Essai de classification des eaux siliceuses d'origine thermominérale. Pierre Urbain, Institut d'Hydrologie et Climatologie, Paris, France.

Silicon is present in all natural waters, particularly in those of deep-seated origin and occurs in them chiefly as colloidal silica particles. Because of the high pH values of thermal waters, silica in them forms readily SiO_3^{2-} anions, but the presence of complex ions is not excluded. The thermal waters may be classified according to their absolute or relative SiO_2 content. The said two classifications are illustrated by means of examples from among French siliceous thermal waters. Their trace-element content is related to water temperature.

The behaviour of sulphur during fractionation of basic magma. L. R. Wager and E. A. Vincent, Department of Geology and Mineralogy, Oxford, England, and A. A. Smales, Atomic Energy Research Establishment, Harwell, England.

The average sulphur content of the 300 km^3 of basic magma of the differentiated Skaergaard intrusion is estimated from analyses of the chilled marginal gabbro at 50 p.p.m. Immiscible liquid, mainly consisting of copper sulphide, was precipitated in small amounts (0·02 per cent) throughout the lower 2 km of the layered rocks, while later, in the uppermost ferrogabbros, immiscible iron sulphide liquid formed up to 2 per cent of some rocks.

It is shown that the copper sulphide liquid separated when the silicate magma contained 200 p.p.m. Cu and 100 p.p.m. S, and the iron sulphide liquid when sulphur in the magma had risen to 600 p.p.m. (the FeO content being then about 15 per cent).

Estimates of Ni, Co, and Cu in the sulphide liquids at various stages of the fractionation are based upon neutron-activation analyses made on the rocks as a whole, since, with one exception, separation of the actual sulphides proved impossible.

Nickel enters the later iron-rich sulphide liquid more readily than the early copper-rich

liquid, but falls to 1 p.p.m. in the pyrrhotite from a late granitic fraction (which was separated for direct analysis). Cobalt is strongly concentrated in the copper-rich liquid, and moderately so (230 p.p.m.) in the iron-rich liquid and the latest pyrrhotite. Nickeliferous pyrrhotite is not found in the Skaergaard intrusion because the abundant entry of nickel into the early olivine and pyroxene depleted the magma in this element before any immiscible iron sulphide liquid formed.

Comparison of deep-sea and nearshore clays with reference to some minor elements. K. H. Wedepohl, Mineralogisch-petrographisches Institut, Universität Göttingen, Göttingen, Deutschland.

Because of absence of reliable data on the distribution of most of the minor elements in deep-sea sediments, especially from the Atlantic Ocean, new investigations were started by means of d.c.-arc spectroscopy and X-ray fluorescence spectroscopy, using internal standards.

The published information on the abundance of minor elements in shales is revised and supplemented by new data. The averages for shales are used for a comparison between deep-sea and nearshore clays. A remarkable difference between two groups of elements is established:

(a) abundance in shales = in Atlantic clays = in Pacific clays: V, Cr, Ga, Zr, etc.

(b) abundance in shales < in Atlantic clays < in Pacific clays: La, Sc, Y, Zn, Yb, Ni, Co, (Ba), Cu, Pb, Mn, B, (Mo), etc., approximately in order of increasing content.

The factors of enrichment in Pacific clays compared with nearshore clays range from 1·5 to 15. In group (b), the content is reversely proportional to the rate of sedimentation. Weathering products from specially composed rock areas are not believed to produce these abnormal contents in the largest basins, which should rather represent average crust material. Biological processes (large-scale foraminifera production) should yield different element associations. The low vapour pressures of halogen compounds of the concentrated elements might indicate a long-lasting air-contaminating action of volcanic emanations as a probable source of these elements. In group (b), a rather constant ratio of enrichment exists between Atlantic and Pacific clays (1 : 3·7) which may depend on the differences in the rate of sedimentation.

Recherches expérimentales sur quelques aspects de la géochimie de la biosphère. René Weil, Laboratoire de Minéralogie de l'Université, Strasbourg, France.

L'origine biogénétique de nombreux gisements miniers est à l'ordre du jour. Nos recherches expérimentales ont porté sur la possibilité de formation de sulfures métalliques dans les conditions semblables à celles de la biosphère, sans nous préoccuper de l'origine même des cations, seul le soufre étant considéré comme d'origine purement biogène.

Dans une première série de recherches, nous avons fait agir du soufre précipité sur des sels ou des oxydes métalliques, dans le glycérol, à des températures ne dépassant pas 100°. Dans une deuxième série, le soufre est fourni par la cystine. Chaque essai est effectué en double, avec ou sans $CaCO_3$, ce dernier représentant le milieu sédimentaire.

Un certain nombre de sulfures ont été obtenus de cette façon: As_2S_3, Sb_2S_3, Bi_2S_3, CoS, NiS, FeS, NiS_2, FeS_2, CuS, Cu_2S, CdS, ZnS, PbS, HgS, $CuFeS_2$.

Il résulte de nos expériences: (1) La possibilité de la formation directe de nombreux sulfures métalliques à partir du soufre organique. (2) L'inutilité de l'hypothèse de la réduction chimique ou bactérienne des sulfates métalliques. (3) $CaCO_3$ agit généralement comme "tampon" rendant le milieu moins acide. Les fonctions basiques de la cystine agissent dans le même sens.

La formation de sulfure peut s'accompagner de celle de carbonate à partir des radicaux COOH de la cystine: par example, PbS et $PbCO_3$. Les produits obtenus peuvent être extrêmement fins, presque à la limite du domaine des rayons X.

Quelques aspects de la géochimie du chrome. Johanna de Widt, Mineralogisch-Geologisch Instituut, Rijks-Universiteit te Utrecht, Utrecht, Nederland.

La teneur en Cr_2O_3 de l'eau de la mer étant imperceptible, tout le chrome des roches ignées désintégrées entre dans les sédiments (argiles, parties argileuses des grès et des calcaires). Son

caractère réfractaire nous interdit de supposer qu'il soit introduit pendant le métamorphisme. On s'attend donc à ce que la connaissance de la teneur en Cr_2O_3 nous aide à faire la distinction entre les amphibolites-para et les amphibolites-ortho; les unes tiendront la teneur des sédiments, les autres posséderont le même pourcentage que le basalte ou le gabbro.

Cette étude a été effectuée à l'aide de l'analyse spectrographique, une méthode essentiellement celle des additions successives selon Addink, utilisant le courant continu.

Pour les argiles et les ardoises une teneur en Cr_2O_3 est trouvée entre 180 p.p.m. et 300 p.p.m. Donc pour les marnes une teneur en Cr_2O_3 est supposée entre 100 p.p.m. et 200 p.p.m. Les basaltes et les gabbros montrent une variation entre quelques milliers p.p.m. et moins qu'une p.p.m. en Cr_2O_3. En considérant les résultats pour une trentaine d'amphibolites, l'exclusion d'un caractère para pour un amphibolite à une teneur en $Cr_2O_3 > 200$ p.p.m. semble inadmissible. Les sédiments, riches en chrome, sont rares. Le résidu stylolithique d'un calcaire montrait 800 p.p.m. de Cr_2O_3. C'est ainsi que le lessivage des carbonates peut produire une teneur élevée en Cr_2O_3 dans une roche d'origine sédimentaire.

Formation of granite-like anatectic melts by experimental metamorphism of clays. Helmut G. F. Winkler, Mineralogisches Institut der Universität, Marburg/Lahn, Deutschland.

Widespread carbonate-free clays consisting of kaolinite illite and quartz, or of illite and quartz, produce, under isochemical hydrothermal treatment at 2000 atm H_2O pressure and 700°–725°C, an anatectic granite-like melt. It comprises 40–65 per cent by weight of the initial clays and is essentially composed of quartz, K feldspar (with some albite component in solid solution), and a little albite.

In three different clays the proportion by weight is almost the same, viz., quartz : K feldspar : albite ~43 : 49 : 8. The melt is situated almost on the cotectic curve of the system, Q–Or–Ab, for 2000 atm H_2O pressure, as determined by O. F. Tuttle and N. L. Bowen. If sodium chloride (which comprises most of the pore solutions at great depths) is added, the amounts of albite and the albite component in the K feldspar will increase, and the melt becomes more granitic in composition. Compared with the chemical composition of the clays, the melt contains much less Al, Mg, and Fe; these are fixed in sillimanite and/or cordierite.

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GEOCHEMICAL NOTE

Chemical composition of oil-field waters from Apsheron Peninsula, Azerbaidzhan SSR: A summary

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Introduction

The chemical compositions of various types of underground waters can be used as indicators for the presence of petroleum (V. A. Sulin, in Vassoevich (1954)):

(1) Sodium sulphate type ($r\text{Na}-r\text{Cl})/r\text{SO}_4 < 1$)†—The sodium sulphate type of underground waters is a usual representative of uncovered formations and, therefore, is not a favourable indicator for the presence of oil. These waters, however, could be present in the uncovered zones of petroleum deposits.

(2) Sodium bicarbonate type ($r\text{Na}-r\text{Cl})/r\text{SO}_4 > 1$)—The high content of bicarbonates or sodium chloride, negligible sulphate content, and the presence of hydrogen sulphide, naphthenic acids, iodine and other microcomponents, which are characteristic of the oil-field waters, make this kind of sodium bicarbonate underground water a favourable indicator for the presence of petroleum.

(3) Magnesium chloride type ($r\text{Cl}-r\text{Na})/r\text{Mg} < 1$)—In general, the magnesium chloride type of waters is not a direct indicator for the presence of oil. These waters, however, are sometimes found in petroleum deposits.

(4) Calcium chloride type ($r\text{Cl}-r\text{Na})/r\text{Mg} > 1$)—The presence of microcomponents which are characteristically found in oil-field waters (iodine, naphthenic acids, bromine, and boron) and insignificant quantities or absence of sulphates are of considerable importance in deciding as to whether the calcium chloride type of waters is a favourable hydrochemical indicator or not.

The presence of calcium chloride type of waters having high mineralization, but containing considerable amounts of sulphates and devoid of iodine or naphthenic acids, is indicative only of a well-sealed formation.

The specific hydrochemical indicators for the presence of oil include: (a) naphthenic acids—direct hydrochemical indicator; (b) iodine (in high concentrations)—supposedly a direct hydrochemical indicator; (c) bromine—does not have a genetic relationship to oil; however, many oil-field waters characteristically contain high concentrations of bromine; (d) boron—supplementary hydrochemical indicator, which is more common in the bicarbonate type of waters; (e) ammonium—indirect hydrochemical indicator; and (f) barium and strontium—supplementary indicators, which do not have genetic relationship to petroleum.

The dashed areas of Fig. 1, which was prepared by N. I. Tolstikhin (*in* Vassoevich, 1954, p. 112), are occupied by the oil-field waters.

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† r = per cent equivalent.

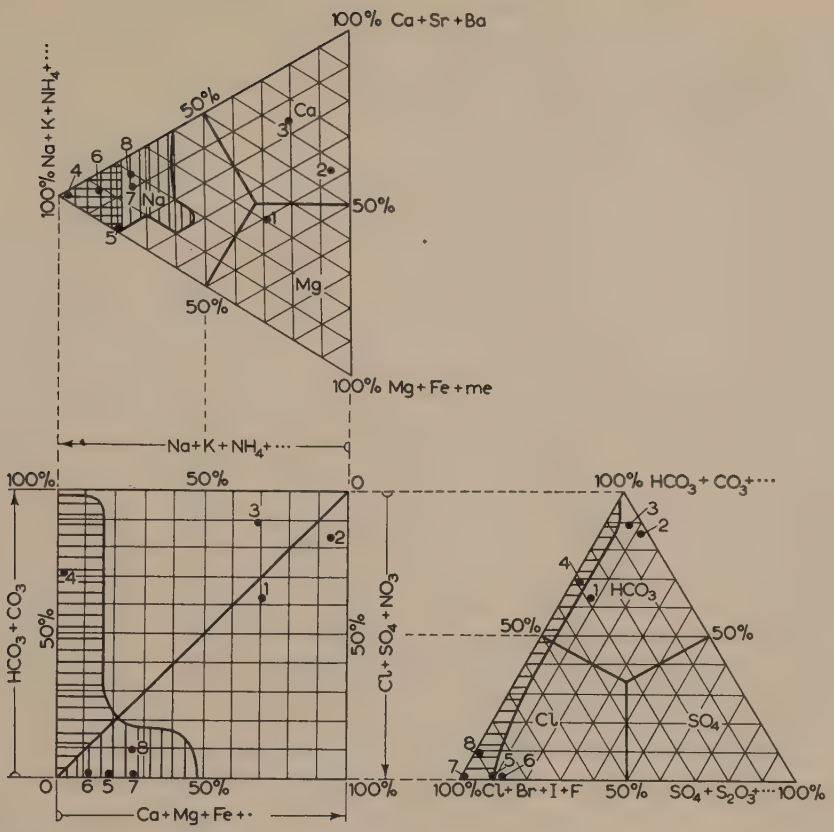

Fig. 1. Graphical representation of chemical composition of oil-field waters—vertically lined areas represent calcium-chloride type waters; horizontally lined, alkaline type. (1) Lake Onega; (2) Darasun mineral spring; (3) Lake Baikal; (4) Oil-field waters from Sakhalin Island, Okha; (5) Ocean; (6) Usol'e Sibirskoye; (7) Ukhta, oil-field waters; (8) Groznyy, oil-field water. (After Tolstikhin, *in* Vassoevich, 1954, p. 112.)

For additional information concerning the classification of natural waters and hydrochemical methods of exploration for oil in the U.S.S.R., the reader is referred to the reviews and summaries prepared by the writer (Chilingar, 1955a,b, 1956, 1957).

Chemical Composition of Oil-field Waters from Apsheron Peninsula, Azerbaidzhan SSR

The chemical composition of oil-field waters from Bibieybat, Balakhany–Sabunchi–Ramany, and Kala petroleum deposits in Azerbaidzhan are presented in Tables 1, 2 and 3. The stratigraphic horizons listed in these tables have been previously described briefly by the writer (Chilingar, 1955c).

In the Bibieybat oil-field waters (Table 1), the sulphate ions are present in negligible amounts. The bicarbonate ion content increases with stratigraphic depth from 1 mg/eq. to 14–16 mg/eq. in Kirmakinskaya formation. The amount of naphthenic acids ranges from 0·2 to 4 mg/eq., with higher content in the lower horizons.

In the oil-field waters of Balakhany–Sabunchi–Ramany deposit (Table 2), the bicarbonate ion content also increases gradually with stratigraphic depth reaching concentration of 10–16 mg/eq. in Kirmakinskaya formation. The naphthenic acids content varies from 0·1 to 0·6 mg/eq.

Table 1. Chemical composition of oil-field waters from Bibieybat petroleum deposit (after MEKHTIEV, 1956, p. 292)

Strata, formation	Salinity (°Bé)	Total mineralization (mg/equiv)	Cl^-	$SO_4^=$	HCO_3^-	Characteristic coefficients	
			(mg/equiv)			S_2	A
I	10·2	334	180	0·6	0·8	17	—
IV	10	367	199	0·7	1·2	22	—
VII	11·3	375	197	0·7	1·1	18	—
X	11·3	364	182	0·3	1	15·10	—
XI	10·2	365	164	0·6	0·7	14·5	—
XII	9·3	330	157	0·4	1	9·7	—
XIII	7·5	249	133	0·3	2·5	1·10	—
XIV sv.	6·9	248	120	0·1	2·8	2	—
XVI sv.	4·2	140	52	0·3	8·8	—	19·5
НКГ	3·9	130	52	0·3	1·6	—	21·4
$НКП_1$	3·5	130	36	0·3	3·8	—	23·6
I—КС	2·5	67	25	0·8	6·3	—	40·9
III—КС	2·2	60	17	0·4	0·3	—	41·3
V—КС	1·9	52	16	0·4	0·9	—	44
$ПК_1$	1·8	46	12	0·3	6·9	—	44
$ПК_3$	1·6	45	12	0·4	5·8	—	36·5

НКГ—Clayey Nadkirmakinskaya formation, subdivided into five strata.
НКП—Sandy Nadkirmakinskaya formation, subdivided into two strata (1, 2).
КС—Kirmakinskaya formation, subdivided into nine strata with total thickness of 220–270 m. Interbedded fine-grained sands, sandstones, clays, and argillaceous sandstones—1 to 5–8 m thick beds.

Table 2. Chemical composition of Balakhany–Sabunchi–Ramany oil-field waters (after MEKHTIEV, 1956, p. 293)

Strata, formation	Salinity (°Bé)	Total mineralization (mg/equiv)	Cl^-	HCO_3^-	Characteristic coefficients	
			(mg/equiv)		S_2	A
Surakhan. fm.	3·51	103	49	2	18·54	0
Stratum I	15	480	238	—	90·00	0
II	12·5–14·2	425	211	1	14·58	0
III	11·5–13·4	427	212	7	15·12	0
IV	10·8	337	166	2	13·80	0
IVa,b	6–10·7	268	130	3	5·58	0
IVc	8·0	249	121	3	4·10	0
IVe	5·7–7·0	213	101	5	0	1·04
V	4·7–5·9	169	77	7	0	6·14
VI	4·3–5·5	169	76	8	0	7·46
VII	4·5	135	57	8	0	11·54
VIII	4·5	137	60	8	0	11·40
IX	4·8	138	60	8	0	11·70
НКП	4·5–5·95	147	65	8	0	8·98
$I\ КС_1$	4·9	93	35	11	0	22·88
$II\ КС_4$		51	13	11	0	47·04
$II\ КС_5$	1·8	51	16	9	0	37·12
ПК	2·0	51	15	8	0	36·38

Strata A, B, C, D, and I (top to bottom)—Surakhanskaya formation.
Strata II, III, IVa, IVb, IVc, IVd, IVe—Sabunchinskaya formation.
Strata V, VI, VII, VIII, IX, X—Balakhanskaya formation (800 m thick); these six sandstone beds are separated by clayey strata 3 to 15 m in thickness.

Table 3. Hydrochemical characteristics of oil-field waters from Kala area (after Mekhtiev, 1956, p. 294)

Strata	Salinity (°Bé)	Total mineralization	Cl^-	$SO_4^=$	HCO_3^-	Characteristic coefficients	
		(mg/equiv)				S_2	A
C	15·5–14·7	509–513	299–262	0·1–1·2	0·3–0·6	21·2–21·36	—
D	15·3–16·8	559–518	281–268	0·1–1·3	0·1–0·7	20·9–22·6	—
II	13·9–14·7	518–437	242–212	0·1–0·9	0·1–0·7	12·5–282·4	—
III	13·9–12·6	470–439	235–219	0·1–0·3	0·1–0·5	18·5–208·2	—
IV	12·7–11·7	422–393	208–203	0·1–0·4	0·2–0·6	17·1–191	—
IVc	12·4–9·6	412–382	206–192	0·1–0·2	0·1–0·2	15·7–17·5	—
V	10·7–8·8	349–297	175–155	0·1–0·1	0·6–1·3	10·7–13·2	—
VI	9·5–8·2	386–282	192–141	0–0·6	0·6–1·5	10·4–12·3	—
$HKГ_1$	5·6–5·5	180–177	88·6–86·6	0–0·1	1·5–1·8	0	0–3·3
HKП	3·7–4·2	181–129	87·1–68·3	0	3·3–5·4	0	0·76–7·5
KC_{1-2}	3·5–3·2	106–96	45·1–39·8	0	4·3–4·6	0	12·3–15·4
KC_{5-6}	2·7–2	75–58	59–16·3	0·1–0·6	4·3–5·5	0	22·3–35·5
KC_{11-12}	2·8–1·9	69–48	19·1–14·7	0·1–0·2	6·4–13·7	0	26–43·4
$ПК_1$	2·3–1·9	82–42	25–14	0·1–0·1	5·5–3·9	0	31–49·3

ПК—Podkirmakinskaya formation, subdivided into five strata. Total thickness up to 130 m.

Table 4 (Mekhtiev, 1956, p. 303) shows the similarity between the marine and oil-field waters. The differences are due to the chemical, microbiological, and hydrodynamic (such as infiltration of atmospheric waters) processes, which gave rise to changes in chemical composition subsequent to burial.

Table 4. Comparison of marine and oil-field waters (after Mekhtiev, 1956, p. 303)

Location	(% equiv)						Palmer's salinity and alkalinity values			
	Cl^-	$SO_4^=$	HCO_3^-	Ca^{++}	Mg^{++}	$Na^+ + K^+$	S_1	S_2	A	a
Bibieybat (VII stratum)	49·58	—	0·42	4·44	5·35	40·21	80·40	18·80	—	0·80
Karachukhur (HKП)	—	0·39	5·82	0·08	0·69	49·23	89·76	—	10·52	1·52
Balakhany–Sabunchi–Ramany (ПК)	31·77	—	19·23	0·81	1·01	48·18	60·06	—	36·38	3·56
Neftechala	49·74	0·23	0·03	11·02	4·70	34·28	66·96	32·98	—	0·06
Caspian sea	34·58	14·51	0·91	3·81	13·81	32·28	64·56	33·62	—	1·82
Ocean	45·22	4·62	0·16	1·77	8·92	39·31	78·6	21·1	—	0·3

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LETTERS TO THE EDITOR

Alpha radioactivity of iron meteorites (second letter)

(*Received* 5 *December* 1957)

We indicate, herein, the results obtained on continuing the study described in previous publications (Deutsch *et al.*, 1956a, b) of the measurement of the α-activity of iron meteorites with the help of nuclear photographic emulsions.

Four meteorites have been studied—Carbo, Toluca, Tamarugal and Thunda—the specimens being exposed in the form of discs of 2 cm diameter and about 0·5 cm thickness. The photographic plates were prepared, immediately prior to use, from an Ilford C2 emulsion in gel form, coated and dried in an atmosphere of 3 months old nitrogen.

That surface of the specimen exposed to the photographic emulsion was turned on a lathe, in a nitrogen atmosphere, the final cutting being done with a diamond point. The meteorites were exposed for a period of 4 months, at a temperature of $-35°$, in a closed recipient containing a nitrogen atmosphere; simultaneously with the exposure of the specimens, other photographic plates were exposed to alpha radiation from a source of known intensity, with the object of obtaining a control for the fading effect (Deutsch and Picciotto, 1957); yet other plates, coated with the same emulsion, were exposed face to face, in order to determine the background effect of the emulsion.

The following table shows the results obtained.

Alpha activity measurements of four iron meteorites (Duration of exposure: 122 days)

	Carbo	Tamarugal	Thunda	Toluca (Hamburg)	Blank plates
Surface observed (cm^2)	6·28	3·14	3·14	6·28	17·5
Alpha count	20	10	11	28	82
(α/cm^2-sec)	$3 \cdot 10^{-7}$	$3 \cdot 10^{-7}$	$4 \cdot 10^{-7}$	$4 \cdot 10^{-7}$	$4{\cdot}6 \cdot 10^{-7}$
Minimum expected activity (α/cm^2-sec) from U and Th measurements of Dalton *et al.*					
due to U	$6{\cdot}6 \cdot 10^{-7}$	$5 \cdot 10^{-7}$	$8 \cdot 10^{-7}$	$2{\cdot}9 \cdot 10^{-7}$	
due to Th	$0{\cdot}8 \cdot 10^{-7}$	$6 \cdot 10^{-7}$	—	$9{\cdot}1 \cdot 10^{-7}$	
due to U + Th	$7{\cdot}4 \cdot 10^{-7}$	$11 \cdot 10^{-7}$	$8 \cdot 10^{-7}$	$12 \cdot 10^{-7}$	
From U measurement of Reed and Turkevich due to U		$<0{,}7 \quad 10^{-7}$	$<0{,}7 \quad 10^{-7}$		

The minimum background of the emulsion is one half the activity of the blank experiment plates (Deutsch *et al.*, 1956b), i.e. $2{\cdot}3 \cdot 10^{-7}$ α/cm^2. The average effect above that of the background, due to the meteorites, is therefore of $1{\cdot}5 \times 10^{-7}$ α/cm^2-sec at its maximum, corresponding to $0{\cdot}9 \cdot 10^{-9}$ g/g of uranium in equilibrium with its daughters. This activity is much lower than

that to be expected from the measurements on thorium and uranium of DALTON *et al.* (1953) and confirms the fact that their results were erroneously high, not only for uranium (REED and TURKEVICH, 1955) but also for thorium—at least for the Tamarugal and Toluca (Hamburg) meteorites. A direct radio-chemical determination of thorium in these same specimens is in the process of being carried out.

We wish to express our gratitude to Professor PANETH and Professor UREY for the meteorite specimens, and also for the interest which they have shown in this work.

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A typical parent meteorite body

Reply to comment by H. C. UREY

(*Received* 15 *January* 1958)

I AM indebted to the editors for this opportunity to reply to Professor UREY's criticisms of two papers (LOVERING, 1957a,b) dealing with the nature of a typical parent (primary) meteorite body. In his comments Professor UREY has brought up a number of points which would appear to be mainly based on his personal views concerning the origins of the meteorites. These will not be discussed in this plan but only certain specific matters of fact.

(1) With regard to Professor UREY's criticisms of the second paper (LOVERING, 1957b), I would like to point out that my purpose was to re-examine previously presented evidence for the existence of considerable pressures within the parent meteorite body (BROWN and PATTERSON, 1948; UHLIG, 1954, 1955) in the light of new data and with certain revisions to to the methods of approach. Many of Professor UREY's criticisms are actually criticisms of these previous workers and their conclusions, and for an appreciation of their points of view it is suggested that the original papers be consulted. However it is difficult to understand some of Professor UREY's criticisms of the general conclusion of my paper (that all available evidence suggests a parent body with interior pressures of lunar magnitude) in view of his own independent conclusion that at least some of the "primary" or "secondary" meteorite objects were of lunar mass or greater (UREY, 1956, p. 623).

(2) Elaborate precautions were taken to prevent the possibility of metal (or other phase) contamination of the olivines from stony-iron meteorites. Samples for analysis were obtained by hand picking, under a high-powered binocular microscope, fragments of olivine crystals which were obviously free from contaminating phases (e.g. metal, schreibersite, troilite, magnetite). The inclusion-free hand picked olivine fragments were crushed in an agate mortar, and a powerful hand magnet was used to search for any magnetic material in the powder; however no such contaminating material was detected. It is an interesting point that even though the

Brenham olivine had one of the highest nickel contents observed, a sample of the analysed olivine powder subjected to X-ray investigation did not show any evidence of contaminating phases. On this basis it seems reasonable to conclude that whatever the cause of the observed nickel variation in the pallasitic olivines may be, it does not seem to be due to metal phase contamination.

(3) The equilibrium temperature assumed for the metal/silicate fractionation follows from Lord Rayleigh's (1944) experiments on the formation of the stony-iron meteorites (see also Lovering, 1957a). From these conclusions the maximum temperature at which molten 11 per cent nickel–iron alloy (m.p. about 1800°K) is forced between already crystallized olivine crystals is given by the melting point of this olivine (about 2000°K). Pressure may increase these temperatures a little but it is not considered that pressures of the order of 10^4 atm would cause any major changes. Consequently the maximum, and thus the most reasonable, temperature at which the observed metal/silicate equilibrium in pallasites would be established was about 2000°K.

(4) Professor Urey has commented that if the meteorites cooled to about 700°K over some 10^9 years then nickel diffusion would occur during this time and presumably seriously modify any pre-existing equilibrium nickel fractionations. However it does not seem possible at this stage to calculate just how much diffusion, at continuously decreasing temperature, will modify the nickel fractionations formed at higher temperatures since little relevant data (e.g. nickel diffusion coefficients in metal, silicate and sulphide phases; cooling rate of meteorite body interior, etc.) are available. Some data are available on nickel diffusion coefficients in iron–nickel alloys (Uhlig, 1954) and rough calculations suggest that perhaps significant diffusion of nickel could be operative in the metal phase of pallasites, within the estimated time available, down to temperatures of about 1000°K but probably not lower. No definite figures are available but it seems likely that in the sulphide and, particularly, the silicate phases, significant nickel diffusion would have been effectively restricted at temperatures considerably *higher* than those calculated for the metal phase. Then again the effectiveness of diffusion in modifying nickel fractionations formed at relatively high temperatures depends in the final analysis on the cooling rate of the primary meteorite body interior. It is extremely important, from a number of points of view, that the thermal history of the primary body should be better understood. Allan and Jacobs (1956) have made an important contribution and further studies are currently in progress in this department.

All that can be said at this stage is that the equilibrium temperature previously assumed for the metal/silicate nickel fractionation (~2000°K) may perhaps be somewhat reduced by subsequent nickel diffusion during cooling, although the available data are in no way conclusive. On the other hand there seems to be little likelihood that the lower equilibrium temperature previously assumed for the metal/sulphide nickel fractionation (~1200°K) need be significantly modified following nickel diffusion during subsequent cooling.

Furthermore, if lower equilibrium temperatures are assumed during cooling to about 700°K (as Urey has implied), then in both the cases of the metal/silicate and metal/sulphide nickel fractionations, simple calculations show that the observed fractionations in meteorites are such that even *higher* pressures than those I have previously calculated must be postulated to have operated. In the previous calculations the maximum possible equilibrium temperatures for both fractionations were assumed so that the calculated pressures would not be overestimated.

(5) In the absence of other suitable data I have followed Brown and Patterson (1948) in using simple volume data to estimate the effect of pressure on the equilibrium constant. It was well recognized both by them and myself that such data would allow only first order approximations to be made of pressure effects. Consequently it was only possible to estimate that the operative pressures were within the range of from 10^4 to 10^5 atm.

(6) The average equilibrium constant C for the metal/sulphide nickel fractionation in pallasites and iron meteorites given previously may be calculated from the following data (Table 1) which, except in the iron content of the sulphide, follow directly from information in the previous Table 4 (Lovering, 1957b).

The samples analysed were obtained by drilling the troilite phase in the meteorites using

a tungsten carbide tipped dental drill under a binocular microscope. In this way obvious contamination of the samples by metal phase was reduced to a minimum but it would appear from the considerable variability in the nickel contents of the troilites analysed that some contamination may have occurred from the nickel-rich phosphide phase (schreibersite) which

Table 1. Average concentration (%) of iron and nickel in metal and sulphide phases of pallasites and iron meteorites

	Fe (metal)	Ni (metal)	Fe (sulphide)	Ni (sulphide)	C
Pallasites	88	12	63·6	0·65	0·07
Iron meteorites	92·8	7·2	63·6	0·3	0·06

is commonly intergrown with troilite in meteorites. It seems virtually impossible to prevent such contamination so that the actual nickel content of meteoritic troilite may well be less than the average values used in this present discussion. This in turn suggests that the value of C calculated in this work may well be reduced even further implying that even *greater* pressures were operating than those previously suggested.

(7) The metal/sulphide equilibrium was most likely established at a temperature of about 1200°K. While both metal and sulphide phases in meteorites were still molten, equilibrium distributions of nickel would have been reached relatively rapidly in response to falling temperatures. However once the phases solidified the response would be greatly reduced since diffusion coefficients in the solid phase are generally several orders of magnitude less in solid phases than liquid phases. For example the diffusion coefficient for nickel in solid γ-phase iron alloy at 1000°C is about 10^{-12} cm^2/sec while in liquid iron it is about 10^{-4} cm^2/sec. Perry (1944, p. 86) reports that the eutectic temperature for a solution of 89 per cent iron and 16 per cent sulphide is 970°C (1243°K) so that the best estimate of the temperature at which the metal/sulphide fractionation in meteorites was stabilized is about 1200°K, as given in Table 1 in the paper under discussion. I am indebted to Professor Urey for pointing out an error in Table 6 as published. The metal/sulphide equilibrium temperature should of course read 1200°K and the pressure estimates were based on this temperature.

(8) The evidence suggesting crystallization and cooling of iron meteorites under pressure has been described previously by Uhlig in two important papers (Uhlig, 1954, 1955). In the paper under discussion I reviewed the relevant data and concluded that Uhlig's original estimates of cooling temperatures (~600°K) and pressures (about 10^5 atm) might well be modified to allow for slightly higher cooling temperatures (~700°K) and rather lower operating pressures (something like 7×10^4 atm). Repeating the rough calculations previously published by Urey (1956, p. 628) it appears that even at temperatures as low as 700°K, the time required for the formation of the Widmanstatten pattern in octahedrites is something of the order of 10^8 or 10^9 years. Since 700°K is apparently the *lowest* temperature reached by the iron meteorites in the interior of the primary body, there seems to be ample time available for the formation of the octahedrites.

(12) Professor Urey has endeavoured to explain the evidence for high pressure presented by Uhlig by suggesting that "nickel rich ataxites were formed at high pressures and that the octahedrites were formed at low pressures". However diamonds have only been found in certain coarse types of octahedrites and not in nickel-rich ataxites, an observation which would indicate that nickel-rich ataxites have cooled under somewhat lower pressures than have the octahedrites. Such a conclusion is in agreement with the evidence presented previously (Lovering, 1957a) for the location of the crystallization and cooling sites of the various types of iron meteorites within the core of the primary body.

(9) The uncertainty in the Thomson-Mayne age relations of the olivine and metal phases of the Brenham pallasite was referred to in a footnote in my paper (see p. 254). Furthermore

this uncertainty has no bearing on any of the estimates given for temperatures and pressures within the parent body.

(10) Another interpretation of the significance of diamonds in iron meteorites was presented by Professor Urey (1956) in a paper which appeared when my paper was in the proof stage of publication. No change was made to the proofs, except for the insertion of a reference to his comments concerning graphite pseudomorphs after diamonds in iron meteorites, since it was obvious that our interpretations of the significance of the carbon phases, in terms of the origin of iron meteorites, were quite different.

(11) Apparently Professor Urey has no specific criticism of the differentiation mechanism suggested in the first paper (Lovering, 1957a) to explain the observed variation in nickel contents of the various iron meteorites. However he does comment that, in view of the evidence which he interprets as pointing to chemical fractionation of the iron–nickel in meteorites it is "most unlikely that the entire variation in nickel content is due to fractional crystallization of an iron nickel melt containing 11% nickel". The evidence to which he refers (Urey and Craig, 1953) is concerned only with the *secondary* meteorites, the chondrites, and as such has no direct bearing on the problem of the evolution of the iron meteorites in the *primary* parent meteorite body. Furthermore more recent work by Wiik (1956) and Brown and McKinney (1957) would indicate that other groupings of chondrites might well exist. Just what these reported groupings of chondrites indicate in terms of "chemical fractionation of the iron nickel in meteorites" is very difficult to say. But it is clear that whatever the reason, it can only apply to the evolution of the *secondary* (chondritic) meteorite bodies and does not necessarily have any connection with the evolution of the *primary* iron meteorites in the *primary* meteorite body.

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Hydrothermale und röntgenographische Untersuchungen an gesteinsbildenden Mineralen—IV

Über hydrothermal hergestellten Ägirinaugit

(*Received* 23 *January* 1958)

Im Rahmen der hydrothermalen Untersuchungen an Weilburgiten in Bomben mit Temperaturgefälle (Euler und Hellner, 1958a) berichteten wir vor kurzem über die Herstellung von Andradit (Euler und Hellner, 1958b). Bei den gleichen Versuchen wurden ausser Andradit folgende Neubildungen erkannt: Alkalifeldspäte, Hämatit, Biotit und Ägirinaugit. Über den letzteren soll hier berichtet werden.

Der Ägirinaugit bildete sich aus dem Na-Weilburgit vom Steinbruch Gabelstein bei Balduinstein im Lahngebiet (Lehmann, 1957). Eine Leiste (3 × 3 × 100 mm) dieses Gesteins wurde bei 1000 bar H_2O–Druck einem Temperaturgefälle 600°/410°C unterworfen. Bei 600°C kristallisierten in grosser Anzahl gut ausgebildete kurzprismatische bis nadelige grüne Pyroxene; die Kristalle waren maximal 0,5 mm lang und 0,2 mm dick. Bei der goniometrischen Vermessung wurde oft die Flächenkombination (100), (010), (110), (111), ($\bar{1}11$) gefunden, daneben wurden vereinzelt die Flächen ($\bar{3}12$), (001), (021), ($\bar{1}01$) beobachtet.

Die mikroskopischen Untersuchungen ergaben

$$\alpha = 1{,}725;\ \beta = 1{,}740;\ \gamma = 1{,}760;\ X \wedge c = 27°;\ 2V_Z = 83°;$$

Achsenebene (010); man beobachtet deutlichen Pleochroismus mit X = grün, Y = hellgrün bis gelblich, Z = hellgelb bis grünlich. Alle optischen Daten sind Messergebnisse und nicht z.T. errechnet. Eine Verzwillingung wurde nicht festgestellt. Die Brechzahlen und die Auslöschungsschiefe wurden an orientierten Kristallen bzw. Dünnschliffen für Na-Licht bestimmt. Die Messung von 2 V erfolgte mit dem U-Tisch, die optischen Achsen konnten dabei konoskopisch eingemessen werden. Bei Verwendung der Segmente $n = 1{,}65$ erhielten wir ein gutes konoskopisches Bild von einem 0,27 mm langen und 0,07 mm dicken Kristall mit Hilfe des U-Tisch-Objektivs UM 4 und eines Spezialkondensors für Drehkonoskopie (Leitz, E. Wetzlar). Wegen der Differenz der Brechzahlen des Segments und des Kristalls wurden die am U-Tisch abgelesenen Kippwinkel nach dem Nomogramm bei Tröger (1956) korrigiert.

Wenn man alle optischen Messergebnisse in das Dreistoffsystem Diopsid, Hedenbergit, Akmit bei Winchell (1951) einträgt, dann schneiden sich diese Messwerte praktisch in einem Punkt. Dieser Punkt im Dreistoffsystem entspricht einer Zusammensetzung von 43 Mol.-% $CaMgSi_2O_6$ (Diopsid), 38 Mol.-% $NaFeSi_2O_6$ (Akmit), 19 Mol.-% $CaFeSi_2O_6$ (Hedenbergit); der hier beschriebene Pyroxen ist also ein Ägirinaugit. Das verwendete Dreistoffsystem bei Winchell hat die Anmerkung "based on scanty data"; unsere Messdaten sind ein weiterer Hinweis für die Richtigkeit dieses Dreistoffsystems.

Ausser den optischen Messungen wurde dieser Ägirinaugit auch röntgenographisch mit Hilfe von Dreh-, Schwenk- und "Precession"- Aufnahmen untersucht. Nach Morimoto (1956) kristallisieren nicht alle monoklinen Pyroxene in der für den Diopsid charakteristischen Raumgruppe $C_{2h}{}^6$-$C2/c$, sondern einige, wie z.B. Pigeonit und Klinoenstatit, in der Raumgruppe $C_{2h}{}^5$–$P2_1/c$; der hier beschriebene Ägirinaugit gehört der Raumgruppe $C_{2h}{}^6$–$C2/c$ an. Aus Guinier-Aufnahmen mit $CuK_{\alpha 1}$–Strahlung wurden folgende Gitterkonstanten bestimmt:

$$a_0 = 9{,}806 \pm 0{,}005\ Å;\ b_0 = 8{,}940 \pm 0{,}005\ Å;\ c_0 = 5{,}284 \pm 0{,}005\ Å,\ \beta = 105°34' \pm 5'.$$

Morimoto (1956) teilt Gitterkonstanten für Pigeonit und Augit von Hakoné Volkano (Japan) mit. Auch er fand für beide Pyroxene eine b_0-Gitterkonstante von 8,940 Å.

Über die petrogenetische Bedeutung dieser Versuche am Weilburgit wird gesondert berichtet.

Der *Deutschen Forschungsgemeinschaft* danken wir für eine Sachbeihilfe. Die Firma E. Leitz, Wetzlar, stellte uns den Spezialkondensor für Drehkonoskopie zur Verfügung, wofür ebenfalls gedankt sei.

Mineralogisches Institut R. Euler
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Deutschland.

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BOOK REVIEWS

Recent Research in Climatology (Proceedings of a Conference held at Scripps Institution of Oceanography, La Jolla, California, 25–26 March 1957). Edited by HARMON CRAIG and issued by the Committee on Research in Water Resources, University of California. x plus 121 pp., mimeographed. (Copies available on request from Dr. Harmon Craig, Scripps Institution of Oceanography, La Jolla, California.)

THIS is the second conference at Scripps to be sponsored by the University of California Statewide Committee on Water Resources. For a note about the proceedings of the first one, entitled New Research Methods in Hydrology, see this journal Vol. **13,** No. 4, p. 342, 1957 (issued 1958).

This volume follows the outline and objectives of the first one, in calling attention to new techniques for climatological research and giving some of the information obtained by these new methods. There are fourteen papers; they can be roughly grouped according to four general topics, although several of them would fit into more than one group:

(1) climatologic implications of studies of naturally occurring isotopes in the atmosphere and the sea ("isotope climatology");
(2) glacial and post-glacial climatic history of the U.S.;
(3) effects of carbon dioxide on climate;
(4) radiation balance of the atmosphere.

There is a general bibliography of fifty-four references at the end of the volume in seven subject categories. These not only serve as references for most of the individual articles, but also provide collateral reading for individuals interested in pursuing some of the topics further. Two of the papers have specialized lists of references appended.

EARL INGERSON

ALLAN O. KELLY and FRANK DACHILLE: **Target, Earth: The Role of Large Meteors in Earth Science.** Published by the authors, Pensacola, Florida, 1953. viii + 263 pp., $5.00.

THIS book serves a useful purpose in emphasizing the probable much greater abundance of meteorites during the early stages of the earth's history as compared to recent times. The authors go much too far, however, in ascribing a major role to meteorites in most geologic phenomena right up through the most recent glaciations.

In order to explain as results of meteoric impacts such diverse phenomena as the filling of Lake Bonneville, the origin of deposits of metal, coal and petroleum, and major tectonic features such as the San Andreas fault and the African Rift Valleys, it has been necessary to neglect so many geological facts and well-established theories that much of the book reads like not too carefully prepared science fiction.

Anyone trained in earth science can pick out the fallacies and answer the spurious arguments, but if this book falls into the hands of too many uncritical laymen, popular information in this field will be set back very considerably.

Unfortunately, it does not stand alone in some of these defects. A recent "scientific communication"* neglects completely such factors as geographic and stratigraphic distribution, and chemical composition of all known meteorites in ascribing a meteoritic origin to the Rhodesian–Belgian Congo copper belt and to the Colorado Plateau and Blind River uranium deposits.

EARL INGERSON

* *Econ. Geol.* **52,** 307–310 (1957).

F. Heide: **Kleine Meteoritenkunde.** Second Edition. Springer-Verlag, Berlin, Göttingen, Heidelberg, 1957. vii + 142 pp., 107 illustrations, DM 7.80.

The scientific study of meteorites is now more than a century and a half old, but only two attempts have been made to treat the whole subject in a comprehensive way. Of these Dr. Meunier's *Météorites* (Paris, 1884) gave undue prominence to his own numerous but not very profound publications; on the other hand Professor Cohen's *Meteoritenkunde* was planned in the best style of a German "Handbuch"—and had a fate not uncommon amongst them: it remained unfinished, owing to the death of its author in 1905, and the absence of an index makes the three parts that have appeared awkward to use. Dr. Farrington's less ambitious treatise *Meteorites* (Chicago, 1915) served its purpose much better, but is now out of date. Recent American books on meteorites by H. H. Nininger are obviously intended to awaken interest rather than to satisfy scientists who want to study the subject. It is to be hoped that a Russian treatise on meteorites, by Prof. E. L. Krinov, will appear in an English translation, but the date of its publication is not yet known.

This state of affairs explains why Professor Heide's book, which appeared in 1934 with the modest title *Kleine Meteoritenkunde*, was in spite of its smallness so gladly received by scientists and laymen alike, and why we are certain that a no less hearty welcome will be extended to the second edition, which came out a few months ago. As long as no bigger "Meteoritenkunde" (in Cohen's sense) is available, this little volume of no more than 138 pages of text (including the illustrations) is the best guide to the subject for the serious student as well as for the amateur. The literary skill with which the author has packed the book with a wealth of up-to-date information without making the reading tedious, or too difficult, for the beginner, is one of the outstanding characteristics of this book.

Being a mineralogist, the author speaks as an authority on the questions of the chemical composition and structure of meteorites; but the astronomical viewpoint is not forgotten, and the historical and cultural aspects of the meteoritic phenomena are dealt with in a most attractive way. (One small correction: in the temple of Ephesus the image of the goddess Diana was not a meteorite; but besides this image the temple contained also, as the Acts of the Apostles tell us, a holy object "from the sky," as a remnant of a more ancient cult.) A carefully compiled chapter surveys all information available today concerning meteorite craters. In the discussion of the origin and age of meteorites the results of recent radiochemical investigations are summarized in several tables; throughout the book the author makes use of tables to present a very rich material without over-burdening the text. Another feature deserving special mention are the numerous illustrations; the small size of the book made it necessary to print some of them in a very reduced scale, but as the technique of reproduction is excellent they convey the necessary information even so. In an appendix pictures of tektites are given and the still open question of their origin is briefly discussed.

Since many more of the people interested in meteorites are living today in English-speaking than in German-speaking countries, one is tempted to recommend an English translation of this excellent modern German book which does not seem to have a counterpart in any other language. However, we do not advocate it, for reasons which seem to us valid in many similar cases. It can be assumed that most scientifically minded people, especially students at Universities, know at least a little German; we would advise them, instead of hoping for the appearance of a translation, to procure the German original right away. The tables and pictures will be intelligible to them without any difficulty, and from a study of the text they will not only gain information on meteorites but at the same time an acquaintance with excellent scientific German prose.

F. A. Paneth

Geochimica et Cosmochimica Acta, 1958, Vol. 14, pp. 181 to 182. Pergamon Press Ltd., London

NEWS AND NOTES

International Oceanographic Congress

THE American Association for the Advancement of Science, in co-operation with UNESCO and the Special Committee on Oceanic Research of ICSU, is planning and organizing an International Oceanographic Congress to be held during a two week period from 30 August to 12 September 1959 at the United Nations Building, New York.

The purpose of the Congress is to provide a common meeting ground for all sciences concerned with the oceans and the organisms contained in them. The Congress will be devoted to the fundamentals of the marine sciences rather than to their applications.

It has been agreed by the organizing committee that the Congress will be centred around five symposia on the oceans:

1. The history;
2. The boundaries;
3. The deep sea;
4. Dynamics of organic and inorganic substances;
5. The marine life regime.

1. *The history*—Includes discussions of the shape and structure of the ocean basins, the acting forces and processes, the origin of sea water and marine organisms, the stratigraphy of the deep sea and the climatic record.
2. *The boundaries*—Includes discussions of the coupling of sea and air, sea level, epicontinental sediments, estuarine and nearshore circulation (including the estuarine environment), influence of land masses on the behaviour and distribution of marine organisms, and surface films and their importance in exchange processes.
3. *The deep sea*—Includes discussions of the geochemistry and physics of circulation, stirring and mixing in the ocean, nature and origin of bathypelagic life, distribution of pelagic sediment types (biological and physical interpretations), nuclear processes in pelagic sediments and special characteristics of abyssal organisms.
4. *Dynamics of organic and inorganic substances*—Includes discussions of physical chemistry of sea water, biologically active substances in sea water, primary production, balance between living and dead organic matter in the oceans, exchanges between sea and air, exchanges between sediments and sea water and vertical transport in the ocean.
5. *The marine life regime*—Includes discussions of the paleogeography of marine floras and faunas, biogeographical regions in the sea, evolution and adaptation in the sea, the behaviour of marine organisms as influenced by environmental factors, physiology of marine plants, and the culture of marine organisms as a means of understanding environmental influence on populations.

Each topic for a symposium will be considered for two consecutive days. Three invited lectures will be given each morning. The afternoon sessions will be organized around the morning topics, either in round-table discussions, in seminars or in a series of papers. Several groups may run concurrently. Papers for the afternoon sessions will be selected from those received in response to this and subsequent announcements. Not all papers which have been accepted will actually be presented, but all accepted papers will be available at the meeting in mimeographed form. Titles and abstracts should be submitted as soon as possible and in no case later than 1 February 1959. The completed papers must be submitted by 1 May 1959 in order to allow time for duplication and distribution to the participants in the afternoon meetings

well in advance of the meeting. All papers must have an abstract in a second language of the Congress. Papers may be presented in English, French, German, Russian or Spanish. Simultaneous translations will be available for at least some of these languages.

The organizing committee expects that contemporary advances in the marine sciences, rather than reviews of older published work, will be presented under these broad topics. It is hoped that the younger staff members of the various oceanographic laboratories around the world will be encouraged to attend and to take part in the Congress. In order to assist with their attendance, the committee hopes to obtain funds to help defray the travel expenses of these younger participants. The committee also hopes to be able to contribute towards the travel expenses of the invited speakers at the morning sessions.

This notice should be considered as preliminary. Until further notices are issued, titles and abstracts of papers, which are publicly solicited by this notice, and any other correspondence should be sent to:

Dr. Mary Sears, Chairman,
Woods Hole Oceanographic Institution,
Woods Hole, Massachusetts, U.S.A.

Other members of the Committee on Arrangements for the Congress are: Gustaf Arrhenius, John Cushing, Henry M. Stommel, Fritz Koczy, George S. Myers, Roger Revelle, Gorden Lill, Lionel A. Walford and Dael Wolfle (*ex-officio*)

Seventh National Conference on Clays

The Seventh National Clay Conference will be held on 20–23 October 1958, in Washington, D.C. at the U.S. National Museum in the Natural History Building of the Smithsonian Institution and will be open to all who have a common interest in clays and clay technology. It is sponsored by the Clay Minerals Committee of the National Research Council and is under the Chairmanship of Dr. H. F. McMurdie of the National Bureau of Standards.

A principal theme for the conference will be "Geology of Clay Deposits". However, papers will also be presented on other phases of the broad subject of "Clays and Clay Minerals". A field excursion is planned for Monday, 20 October, to typical clay deposits and soil profiles in northeastern Maryland and northern Delaware. A guided tour to the National Bureau of Standards is being arranged for the afternoon of the 22nd. Complete details of the programme will be announced in August.

The programme chairman is Dr. John G. Cady, Soil Survey Laboratory, Plant Industry Station, U.S. Department of Agriculture, Beltsville, Maryland, U.S.A.

Canyon Diablo I meteorite

The undersigned has a considerable quantity of the Canyon Diablo I, Coconino Co., Arizona meteorite in the form of (a) metallic turnings and (b) oxide (so-called "iron shale"). This material is offered *free of charge* to accredited laboratories, or their personnel, for research on geochemical, cosmochemical or meteoritic problems. Applications should be addressed to John D. Buddhue, 1210 No. Arroyo Blvd., Pasadena 3, California, U.S.A. Please state the kind and approximate quantity of material desired.

John D. Buddhue

Geochimica et Cosmochimica Acta, 1958, Vol. 14, pp. 183 to 184. Pergamon Press Ltd., London

PAPERS TO BE PUBLISHED IN FUTURE ISSUES

Hitoshi Sakai and Kazuo Sato: Isotopic composition of the common lead of Japan

Gregor Junk and Harry J. Svec: The absolute abundance of the nitrogen isotopes in the atmosphere and compressed gas from various sources

P. W. Richardson and H. E. Hawkes: Adsorption of copper on quartz

D. M. Anderson and H. E. Hawkes: Relative mobility of the common elements in weathering of some schist and granite areas

R. Coulomb, H. Goldsztein and M. Le Mercier: L'uranium dans quelques granites français

F. M. Rainwater and W. F. White: The solusphere—its inference and study

Stanko Miholic: Radioactive waters from sediments

W. Ernst, K. Krejci-Graf und H. Werner: Parallelisierung von Leithorizonten im Ruhrkarbon mit Hilfe des Bor-Gerhaltes

Earl Ingerson: The next decade in geochemistry

R. J. W. McLaughlin: Geochemical partition in two illitic clays

Warren Hamilton: Information needed with analytical data

Johan Moum and I. Th. Rosenqvist: Hydrogen (protium)–deutrium exchange in clays

James P. Forsman and John M. Hunt: Insoluble organic matter (kerogen) in sedimentary rocks

Edward C. Walker, Frank Cuttitta and Frank E. Senftle: Some natural variations in the relative abundance of copper isotopes

A. E. Ringwood: The constitution of the mantle—II. Further data on the olivine–spinel transition

A. E. Ringwood: Constitution of the mantle—III. Consequences of the olivine–spinel transition

S. Ďurovič: Contribution to the lognormal distribution of elements

Marjorie Hooker: Data of rock analyses—IV. Icelandic periodical and serial literature

R. W. Stoenner and J. Zähringer: Potassium–argon age of iron meteorites

H. Sakai and H. Nagasawa: Fractionation of sulphur isotopes in volcanic gases

H. F. Phillips and I. A. Breger: Isolation and identification of an ester from a crude oil

Robert F. Conley and W. M. Bundy: Mechanism of gypsification

Erik Eriksson: On the isotopic composition of the ammonia and the nitrate ion in rain

E. L. Krinov: Some considerations of tektites (*Tektites Symposium*)

Virgil E. Barnes: Properties of tektites pertinent to their origin (*Tektites Symposium*)

Alvin J. Cohen: The absorption spectra of tektites and other natural glasses (*Tektites Symposium*)

John S. Rinehart: Impact effects and tektites (*Tektites Symposium*)

Carlos M. Varsavsky: Dynamical limits on a lunar origin for tektites (*Tektites Symposium*)

William A. Cassidy: Achondrite investigations and their bearing on the origin of tektites (*Tektites Symposium*)

Irving Friedman: The water, deuterium, gas and uranium content of tektites (*Tektites Symposium*)

George R. Tilton: Isotopic composition of lead from tektites (*Tektites Symposium*)

W. H. Pinson, Jr., L. F. Herzog, H. W. Fairbairn and R. F. Cormier: Sr/Rb age study of tektites (*Tektites Symposium*)

William D. Ehmann and Truman P. Kohman: Cosmic-ray-induced radioactivities in meteorites—I. Chemical and radiometric procedures for aluminium, beryllium and cobalt (*Tektites Symposium*)

WILLIAM D. EHMANN and TRUMAN P. KOHMAN: Cosmic-ray-induced radioactivities in meteorites—II. Al^{26}, Be^{10}, and Co^{60} in aerolites, siderites and tektites (*Tektites Symposium*)

T. ISAACS and R. ROY: The α–β inversions in eucryptite and spodumene

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G. KULLERUD and G. DONNAY: Natural and synthetic ferroselite

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H. G. F. WINKLER and H. VON PLATEN: Experimentelle Gesteinsmetamorphose—II

R. M. GARRELS and C. R. NAESER: Equilibrium distribution of dissolved sulphur species in water at 25°C and one atmosphere total pressure

SAYED A. EL WARDANI: Marine geochemistry of germanium and the origin of Pacific pelagic clay minerals

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It is 120 years since W. H. Perkin was born, and 102 years since he made his great discovery of mauveine during the Easter vacation in 1856—the first synthetic organic dye to be used extensively in dyeing, an achievement which led ultimately to the virtual supersession of natural dyes by synthetic ones.

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